VOL. XXXIII. JUNE, 1905. No. 6.

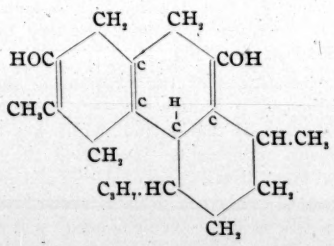
AMERICAN

CHEMICAL JOURNAL

CONTRIBUTION TO THE QUESTION OF THE CONSTITUTION OF ABIETIC ACID.

BY H. ENDEMANN.

The relation between abietic acid and reten was first considered by Tschirch and Studer,[1] who presented the following formula:



According to this, abietic acid should contain 2 hydroxyl groups and not 1 carboxyl group, as was formerly believed to be the case. The position of the methyl groups is, confessedly, arbitrary. However, the chief object of the two workers was

[1] Centrbl., 1903, ii, 1179.

to call attention to the relationship between reten and abietic acid; they did not offer any experimental facts but pointed out that the fossil resin reten is found in the soil of ancient pine forests.

A. Vesterberg[1] went one step further and prepared reten from abietic acid, by distillation with sulphur.

Both results point, therefore, to a relation between abietic acid and reten or another phenanthrene derivative, but it is, at present, by no means certain, even in the light of my own results, whether the third ring of the phenanthrene nucleus is originally present or whether it has not been formed from two aliphatic chains during the long period of time required for the production of reten in the soil, or even during the violent reaction with the sulphur in the retort. For the present I will formulate my results in accordance with the current views.

Abietic Acid Contains One Carboxyl Group.

Abietic acid heated at 160°, in a sealed tube, with excess of acetic anhydride, produces an oil, which can be freed from acetic acid and anhydride by protracted treatment with water, in which the oil is insoluble.

This oil is then saponified by alcoholic potassium hydroxide and the resulting product distilled with phosphoric acid and steam, in the apparatus previously described by me,[2] to recover the combined acetic acid.

Under the conditions of the experiment abietic acid is slightly volatile and it became necessary, therefore, to determine the acid value of this portion, which was accomplished by several blank experiments. Deducting the value so obtained, it was found that 1 gram of abietic acid combined with acetyl sufficient to form 0.207 gram of acetic acid, *i. e.*, for 1 molecule of abietic acid 1 molecule of acetic acid was obtained.

This points conclusively, therefore, to the assumption that abietic acid is really an acid and does not contain 2 hydroxyl groups as Tschirch and Studer state.

[1] Ber. d. chem. Ges., **36**, 4300 (1903).
[2] Industrial Record, 1875. American Chemist, February, 1876.

Oxidation of Abietic Acid by Permanganic Acid in Acid Solution.

Abietic acid has been treated with oxidizing agents before, but usually the result has been a more or less far-reaching decomposition. Thus it is stated that abietic acid yields, with potassium permanganate, carbon dioxide, formic and acetic acids, while with chromic acid the product is chiefly acetic acid with some trimellitic acid.

Potassium permanganate, in strongly alkaline solution, acts less vigorously, so that by this means Mach obtained an acid with the formula $C_{19}H_{16}O_3$, which also indicates an extensive resolution of the original molecule.

Working in an acid solution, it was ascertained that, under certain conditions, products of definite composition could be obtained with less decomposition of the original compound. Ten parts of abietic acid are converted into the sodium salt, by heating with the requisite quantity of sodium hydroxide solution.

Fifteen parts of potassium permanganate are dissolved in so much water that, on cooling with ice, the salt remains in solution; an equivalent amount of sulphuric acid is then added.

The abietic acid solution is diluted to approximately the same volume as the permanganate solution, the two are thoroughly cooled with ice and then quickly mixed. The mixture at first becomes quite thick, owing to the separation of abietic acid, but it speedily becomes more mobile and manganese peroxide separates.

The quantity of ice in this solution should be ample to keep the mixture cold for some time, for heat is evolved during the reaction. The mixture is allowed to stand until the permanganic acid is completely reduced.

Sodium carbonate or hydroxide is now added, in slight excess and the whole is heated to boiling. The insoluble manganese oxides are filtered and the solution is evaporated.

When sufficiently concentrated, acid causes the precipitation of a resinous mass. On concentrating the supernatant liquid more of this resin is obtained. During the evaporation the

solution emits an odor resembling that of the lower fatty acids.

The resinous precipitate has a very decidedly bitter taste and was found to consist of two acids, which may be separated by their own varying solubility and by that of their salts.

An incomplete separation may be made by treating the mass with benzene, which, if not in too large excess, will dissolve one constituent almost wholly, this has a very intensely bitter taste; the residue contains another acid less bitter than the first.

The more soluble compound is completely separated from the residue by boiling it with barium hydroxide, in excess, cooling and filtering. The filtrate is then concentrated on the water-bath; when the salt commences to separate on the surface, the liquid is allowed to cool, again filtered and finally evaporated to dryness. This yields the barium salt of the acid less soluble in benzene.

The same acid may also be obtained, practically free from the other, by extracting the resinous precipitate repeatedly with benzene, dissolving the residue in alkali, boiling to remove all benzene and then reprecipitating the free acid. This removal of benzene by boiling is necessary, because the acid, although very sparingly soluble in benzene, is itself a good solvent for the latter, which it retains tenaciously. This affinity for solvents is, perhaps, the reason why, from most media, I did not succeed in obtaining the acid in a crystalline state. It may, however, be obtained in small crystals by the slow evaporation of its aqueous solutions, the most favorable condition being, apparently, a low temperature. The crystals generally form arborescent masses.

Other solvents such as epichlorhydrin, certain esters, chloroform, carbon tetrachloride, or carbon disulphide, leave the acid in an amorphous state, probably for the reason given above. Prolonged heating, at temperatures much above the boiling-points of the solvents, was necessary in order to remove the last traces of them from the acid. Acetone leaves the pure acid microcrystalline. Strong alcohol cannot be used as a solvent because the acid esterifys very readily, even at the ordinary

temperature. This is evident from the fact that an alcoholic solution requires less and less sodium hydroxide for neutralization the longer it is allowed to stand. Two hours, at the ordinary temperature, are sufficient to raise the apparent equivalent of the acid 50 per cent. An acetone solution, however, can be used for the purpose of determining the equivalent of the acid acidimetrically. The acid is insoluble in petroleum ether and may be precipitated from the solutions of such solvents as will mix with petroleum ether and be freed from the other solvents and unchanged abietic acid, by treating with petroleum ether, in a Soxhlet apparatus.

The second acid is also insoluble in petroleum ether, but both dissolve, to some extent, particularly if the petroleum ether contains resins in solution and also in the presence of terpenes, or fatty substances. After being precipitated and washed in a Soxhlet apparatus for a considerable time, by petroleum ether, the acid forms a non-caking, sandy mass.

The bases with which the acid was combined are removed only with difficulty. After drying in air it melts at 80° and loses $1H_2O$, after which it melts at 111°–113°.

Analysis:

0.1673 gram substance gave 0.4189 gram CO_2 = 68.29 per cent carbon.

0.1673 gram substance gave 0.1275 gram H_2O = 8.54 per cent hydrogen.

This agrees quite well with an acid of the formula $C_{16}H_{24}O_4$. The specimen was not entirely free from ash.

The average composition, deduced from 6 analyses of subsequent preparations, was:

	Calculated for $C_{16}H_{24}O_4$.	Found.
C	68.57	68.59
H	8.64	8.56

This substance has, therefore, been produced from abietic acid by the elimination of the group C_2H_4 and the addition of O_2. It is a dibasic acid, with the equivalent = 139 (theory 140) as determined by titration in acetone solution; this corresponds to the molecular weight 280, for the formula $C_{16}H_{24}O_4$.

It forms an oily *diacetyl* compound, which was examined for acetic acid.

In boiling alcoholic solution the acid gives a precipitate with lead acetate. The percentage of lead in these precipitates, even when they were made from the same preparation is, however, not constant, perhaps because the acid has a great affinity for alcohol and forms, in part, an ester acid, the lead salt of which may, therefore, be present in the neutral lead salt. The formula $C_{16}H_{22}O_4Pb$ required 42.68 per cent of lead. The values obtained were: 41.40, 39.04, 36.69 and 36.4.

The acid, separated from the lead by hydrogen sulphide, always contains much sulphur and this method can, therefore, not be recommended for purification.

The acid is freely soluble in baryta water, even in the ratio 1 molecule barium hydroxide : 2 molecules of the acid. If this solution is boiled, a precipitate is formed, but if it is allowed to evaporate spontaneously it drys to a gummy mass.

If excess of barium hydroxide is used, *i. e.*, more than 1 molecule : 1 molecule of the acid and the solution is boiled, no precipitate is formed even after the excess of barium hydroxide has been removed. On slow evaporation crystals of the salt separate. They appear, under the microscope, as short columns, aggregating to arborescent masses. This salt, after drying at 90°–95°, lost $3H_2O$ at 105°. It contains 33.06 Ba (33.07 calculated).

The second acid formed is found in the benzene solution, together with some of the first acid. It contains 1 oxygen atom less than the latter, *i. e.*, it contains the aldehyde group CHO in the place of CO_2H. Using the proportions of abietic acid and permanganic acid given above, it is the predominant product. It speedily reduces alkaline solution of a silver salt and also gives the aldehyde reaction with Schiff's reagent. The barium salt is difficultly soluble and may be used for the purification of the acid. The lead salt is soluble in alcohol, if it is prepared in boiling alcoholic solution, as described above.

For final purification the free acid is dissolved in benzene, precipitated and finally washed with petroleum ether, in a Soxhlet apparatus. The acid is generally obtained in an

amorphous state, the reason being, probably, the same as in the case of the other acid. From acetone solution it is deposited as a crystalline mass. I have not been able to obtain crystalline salts of this acid and yet it is a chemical individual, for the analyses invariably show the uniformity of the material and fractional precipitations do not exhibit such discrepancies as would suggest a mixture.

The dicarboxylic acid first described is quite soluble in water, indeed the resinous acid, which is recovered by the evaporation of the solution from which the crude mixture of the resins had been precipitated, is almost all dicarboxylic acid.

The aldehyde acid is quite sparingly soluble in water and stands about midway between the dicarboxylic acid and abietic acid, which is not absolutely insoluble.

For analysis the acid was dried at 100°, even at this temperature anhydride seems to form, though to a very limited extent.

	Calculated for $C_{18}H_{24}O_3$.	Found. I.	II.
C	72.66	72.72	72.95
H	9.17	9.00	9.01

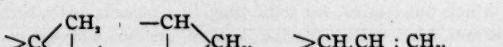
The acid, dried at 105° for several hours, gave:

	Calculated for anhydride.	Found.
C	75.36	74.11
H	9.11	9.15

The equivalent of the acid was ascertained by titration in acetone. Its melting-point is very easily affected by impurities. When highly purified it melts at 188°.

From the above results it follows that abietic acid contains a side chain C_4H_6, constituted as $.CH : C_3H_4$. Under the influence of an oxidizing agent the double bond is resolved and the CH becomes first CHO then CO_2H.

For the complex C_3H_4 three groupings are possible, *viz.*:



Recently, Tschirch and Studer have stated that they have been able, after much labor, to separate three abietic acids, α, β and γ, of which the last two have a tendency to pass into the α.[1]

The most unstable would be $:CH.CH:CH_2$ and it could easily be understood how, under the influence of heat, it could condense into either of the other two, while it is less likely that these, when once formed, should change their constitution spontaneously.

However this may be, if there are three so nearly related I should think that commercial rosin contains all three groupings.

In order to verify still further the above results and conclusions, I have attempted to ascertain what had become of the group C_3H_4, which had been eliminated from the abietic acid. Starting with abietic acid, which had been prepared by saturating an alcoholic solution of rosin with hydrochloric acid and collecting the crystallized acid, I oxidized in the manner described above and used the mother-liquor from the precipitation of the crude acids. This was concentrated and the sulphates allowed to crystallize. The syrupy residue was then examined for a possible compound. After a series of unsuccessful experiments it was found that, when calcium chloride was added in excess and the calcium sulphate filtered off, a copious precipitate was formed by boiling the filtrate. This was thoroughly washed and, after drying, was found to contain 31.12 per cent calcium oxide. The calcium salt was suspended in water and oxalic acid added equivalent to the calcium found. The filtered liquid was then evaporated to dryness and the residue extracted with ether. On spontaneous evaporation, long needles of the acid were deposited.

From the percentage of calcium in the precipitate it was surmised that the acid thus formed was malonic acid. In order to verify this, it was converted into the diacetyl compound, which was heated, for some time, in a paraffin-bath, somewhat above 100°. The residue became yellow and dissolved in

[1] Centrabl., 1903, ii, 1178.

acetic acid, giving a yellow solution possessing the characteristic yellowish-green fluorescence. The acid is, therefore, malonic acid and is produced from the nucleus present in the crystallizable acid and forming .

Using commercial rosin, malonic acid is likewise formed, but in smaller quantity. If more permanganate is employed than above stated, the malonic acid may disappear entirely, which shows that malonic acid is destroyed by free permanganic acid.

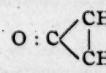
A blank experiment with malonic acid showed it to be easily oxidized by free permanganic acid. The decomposition is accompanied by the evolution of carbon dioxide. The reaction was not followed further, but besides malonic acid there are formed :

1. Syrupy acids.

2. An aromatically odoriferous, neutral substance. As yet, none of these have been identified.

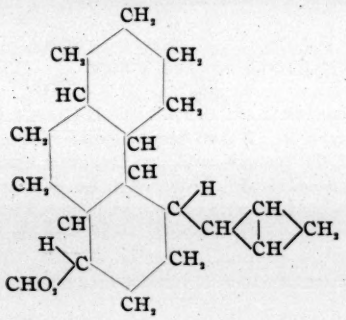
3. A volatile acid, to the extent of about 2 per cent, which consists, in part, of acrylic acid. (Ready absorption of bromine with formation of a bromine addition-product, crystallizing in large hexagonal plates.) When known, these will lead eventually to the constitution of the isomeric acids, by determining the position of the atoms in the group C_3H_4.

I consider it possible that the rosin in turpentine, as obtained in nature, contains the group $:CH.CH:CH_2$, which would form acrylic acid and that the subsequent treatment, necessary for the production of commercial terpene and rosin, causes a condensation of this group into the one forming malonic acid, another one perhaps forming a ketone :



I am not prepared, as yet, to discuss these questions, but expect to do so later. Considering, now, the bearing of this in-

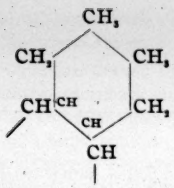
vestigation upon the formula of abietic acid and accepting the general opinion that abietic acid is a reten derivative, the formula must be written as follows:



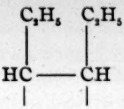
The positions which I have selected for these two side chains are such as to indicate the relation of the acid to reten and they agree with its formula, as determined by Bamberger and Hooker. The acid would be, therefore, a derivative of a fully hydrogenated phenanthrene, wherein 1 atom of hydrogen is replaced by the carboxyl group and 1 by the group C_4H_5.

On this assumption the two resin acids formed would be tetradecahydrophenanthrenal carboxylic acid, $C_{16}H_{24}O_3$, and tetradecahydrophenanthrenedicarboxylic acid, $C_{16}H_{24}O_4$. Acids of the formula $C_{20}H_{30}O_2$ would, perhaps, have the side chain C_4H_7 and form propionic acid by oxidation. During the first stages of their production these acids are only partly in the free state. Another portion is in the form of a mixed anhydride, from which the free acids are produced by hydrolysis, whereby, on the one hand, the resinous acids described are formed and, on the other hand, malonic acid etc.

The possibility that abietic acid is, perhaps, not quite so closely related to phenanthrene and that all the rings given in the formula were not originally present, but that open chains, such as



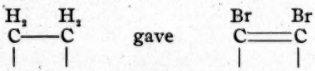
or



were present, makes it necessary to consider the possible existence of a double bond between two of the carbon atoms.

Abietic acid is not very well adapted for the investigation of this point because a double bond exists in the side chain, but this is not the case with the dicarboxylic acid. This dibasic acid is dissolved in chloroform and excess of bromine added (3 : 2 by weight). After 2 days' standing in the cold, the hydrobromic acid which has been formed is shaken out with water and determined, while the acid in the chloroform is recovered by evaporation.

It was found that, for 2 atoms of bromine which had combined with the dicarboxylic acid, 4 molecules of hydrobromic acid had been formed. The reaction, therefore, was not only one of substitution but also one of condensation between two carbon atoms, now connected by a double bond :



This experiment is not absolutely convincing, but, so far, no facts have been brought out incompatible with the formula presented.

The many peculiarities in reactions and properties of the substances derived from rosin, must strike all those familiar with them, as presenting decided similarities and suggesting a close relationship to the bitter principles from hops. This is also observed in their action as preservatives, especially when the destruction of the organisms of acetic and lactic fermentations are concerned. Humulic acid and my dicarboxylic acid differ in composition by CH_4, suggesting the presence of a pen-

tane ring with 1 double bond, already demonstrated,[1] in the place of a hexane ring. On this I shall report later.

In conclusion I wish to state that I have been very industriously helped in these investigations by my assistant, Mr. John W. Paisley, who deserves my sincere thanks.

Since writing the above I have noticed a paper by T. H. Easterfield and G. Bagley,[2] in which they also formulate abietic acid as a decahydrophenanthrene derivative, but with two double bonds, two of the hydrogen atoms being replaced by methyl and isopropyl. In all cases the assumption of the presence of these groups is based upon the reten formula, in which their presence has been recognized.

According to my investigation these groups are not originally present in abietic acid, but must be considered as being formed from the side chains, by the action of reducing agents and abietic acid itself must be considered as a tetradecahydrobutenylphenanthrenecarboxylic acid.

THE APPROXIMATE COMPOSITION OF THE HYDRATES FORMED BY CERTAIN ELECTROLYTES IN AQUEOUS SOLUTIONS AT DIFFERENT CONCENTRATIONS.

[TENTH COMMUNICATION.]

BY HARRY C. JONES AND H. P. BASSETT.

Nine papers[3] have already been published by Jones and his co-workers in this laboratory, on the combination of solvent and dissolved substance in solution. In this, the tenth paper, the approximate composition of the hydrates, formed by a

[1] Lintner and Schnell: Centrabl., 1904, i, 1227.

[2] J. Chem. Soc., 85, 1238 (1904).

[3] Jones and Chambers: THIS JOURNAL, 23, 189 (1900). Chambers and Frazer: *Ibid.*, 23, 512 (1900). Jones and Getman: *Ibid.*, 27, 433 (1902). Jones and Getman: Z. physik. Chem., 46, 244 (1903); Phys Rev., 18, 146 (1904). Jones and Getman: THIS JOURNAL, 31, 303 (1904). Jones and Getman: Z. physik. Chem., 49, 385 (1904). Jones and Getman: Ber. d. chem. Ges., 37, 1511 (1904). Jones and Getman: THIS JOURNAL, 32, 308 (1904). Jones and Getman: *Ibid.*, 32, 308 (1904).

number of electrolytes in water, at different concentrations, is calculated.

In an earlier paper Jones and Getman[1] pointed out *a relation between the lowering of the freezing-point produced by electrolytes and their water of crystallization.* This relation was shown to hold for a large number of chlorides, bromides, iodides and nitrates. Indeed, for about 40 electrolytes with larger and smaller quantities of water of crystallization. The discovery of this relation confirmed us in the conclusion, reached much earlier by one of us,[2] that the abnormal freezing-point results produced by the electrolytes, especially in concentrated solutions, was due to a combination between the solvent and the substance dissolved in it.

Indeed, this conclusion seems to be almost a necessary consequence of the above relation. *If hydrates are present in such solutions, those substances that form the most complex hydrates in solution would be the substances that would crystallize from solution with the largest amounts of water.* This is the same as to say that those substances which, in solution, have the greatest power to combine with water, would be the ones that would bring with them the largest amounts of water out of solution.

We should, however, not expect the two phenomena to be exactly proportional to one another, because the actual shape of the molecules which build up the crystal would also be a conditioning factor in determining the exact number of molecules of water with which any given substance would crystallize.

The best we could hope to discover would be a general, qualitative relation between the lowering of the freezing-point and the water of crystallization. That such a relation actually exists can be seen by consulting Figs. I. to IV.

The data that are incorporated in these curves have already been published.[3]

In Fig. I., the results that have been obtained for the various chlorides, are plotted, as far as could be done on one sheet, without undue crowding. The abscissae are concentra-

[1] Z. physik. Chem., **49**, 385 (1904).
[2] Jones: THIS JOURNAL, **23**, 89 (1900).
[3] *Ibid.*, **31**, 303 (1904). Z. physik. Chem., **46**, 244 (1903); **49**, 385 (1904).

tions expressed as gram-molecular normal, the ordinates are molecular lowerings of the freezing-point. The chlorides of

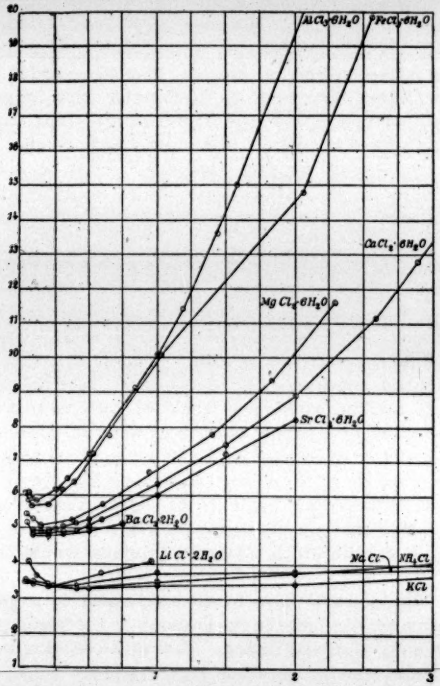


Fig. I.

sodium, potassium and ammonium, which crystallize without water, give the smallest lowering of the freezing-point.

The chloride of lithium, with 2 molecules of water of crystallization, gives considerably greater lowering of the freezing-point of water than the chlorides which have no water of crystallization.

When we pass to barium chloride, which contains 2 molecules of water of crystallization, it gives a greater lowering of the freezing-point than lithium chloride, with the same amount of water of crystallization. It must, however, be remembered in this connection that lithium chloride is a binary electrolyte, yielding only 2 ions, while barium chloride is a ternary electrolyte—each molecule dissociating into 3 ions.

Strontium, calcium and magnesium chlorides all crystallize with 6 molecules of water and all give freezing-point lowerings of the same order of magnitude.

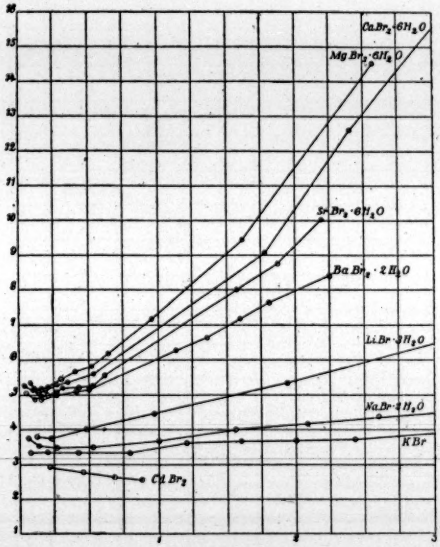


Fig. II.

Aluminium and ferric chlorides contain 6 molecules of crystal water, yet they show much greater lowering than the ternary chlorides with 6 molecules of water of crystallization. This is

to be accounted for by the fact that the chlorides of iron and aluminium are quarternary electrolytes—each molecule dissociating into 4 ions.

Turning to Fig. II., relations, similar to those pointed out above, are seen to exist for the bromides. Sodium bromide,

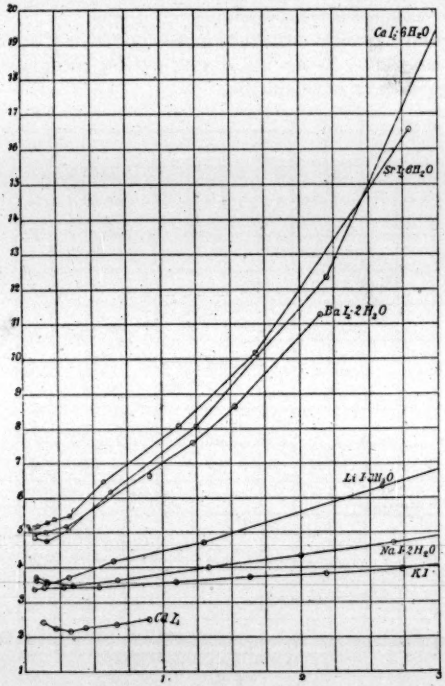


Fig. III.

unlike sodium chloride, crystallizes with 2 molecules of water. It falls considerably above potassium bromide, just as we should

expect it to do. Lithium bromide, with 3 molecules of crystal water, occupies a still higher position in the figure. Passing to the ternary bromides, barium bromide, with 2 molecules of water of crystallization, shows greater lowering than the binary electrolyte, lithium bromide, as we should expect, it also gives considerably smaller lowering of the freezing-point than strontium, calcium and magnesium bromides, each with 6 molecules of water of crystallization.

Relations of an exactly similar character are shown by Fig. III., for the iodides.

The results plotted in Fig. IV., for the nitrates, present cer-

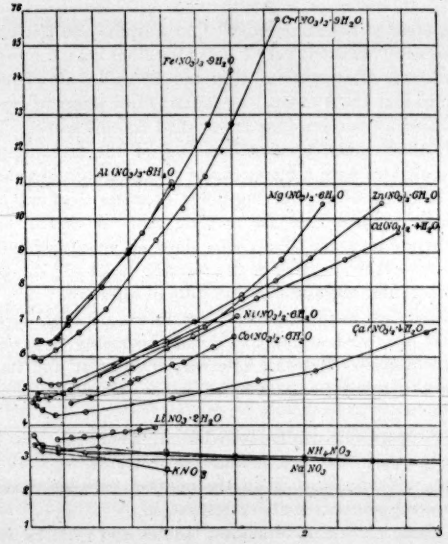


Fig. IV.

tain features of special interest. The nitrates without water of crystallization, sodium, ammonium and potassium, give the

smallest lowerings of the freezing-point. Lithium nitrate, with 2 molecules of crystal water, gives considerably greater lowering than the alkali nitrates.

Calcium nitrate crystallizes with 4 molecules of water and occupies a position in the figure about midway between the alkali nitrates without crystal water and a number of nitrates, each with 6 molecules of water of crystallization. Manganese nitrate, of all the nitrates studied, gives smaller lowerings than we should expect. We have repeated the experiments with this substance, to see if some error has not found its way into this part of the work.

The nitrates of a number of metals, each containing 6 molecules of water of crystallization, give lowerings of the freezing-point of the same order of magnitude and the curves for these substances fall very closely together on the figure.

The nitrates of aluminium, iron and chromium are of special interest, in that these substances contain more water of crystallization than any others thus far studied in this work. They not only show much greater lowering of the freezing-point than the nitrates with 6 molecules of crystal water, but show a greater lowering of the freezing-point of water than any other salts which we have thus far investigated. A careful study of this nitrate diagram, alone, will show an unmistakable relation between the lowering of the freezing-point and the water of crystallization possessed by the salts in question.

Relations such as those pointed out above, between *different salts of the same acid*, are all that could reasonably be expected to exist. Certain relations, however, of interest and importance in this connection, are found *between the salts of different acids*.

If we compare the results plotted in curves in Figs. I. to IV., for the chlorides, bromides, iodides and nitrates, we shall find abundant evidence bearing on the relation between freezing-point lowering and water of crystallization.

Take those chlorides, bromides, iodides and nitrates which crystallize without water; they all show a molecular lowering of between 3 and 4 and this increases very slightly, if at all, with the concentration.

As far as the comparison can be carried, lithium chloride, with 2 molecules of water, gives less lowering than lithium bromide or lithium iodide, with 3 molecules of water and just about the same lowering as lithium nitrate with 2 molecules of water of crystallization.

Lithium bromide, with 3 molecules of water, gives just about the same lowering as lithium iodide, which has the same amount of water of crystallization.

Sodium bromide, with 2 molecules of water, gives very nearly the same lowering as sodium iodide, which has the same number of molecules of water of crystallization.

Barium chloride has the same number of molecules of water of crystallization as the bromide and iodide. Since barium chloride has only a slight solubility in water, comparison of freezing-point lowerings must be limited to dilute solutions. The freezing-point lowerings of the three salts are just about the same in the dilute solutions, although in the more concentrated solutions the iodide shows greater lowering than the bromide.

If we compare the chlorides, bromides and iodides of the alkaline earths, which contain each 6 molecules of water of crystallization, we shall find that the lowerings of the freezing-point produced by them are all of the same order of magnitude. We shall, however, see that the bromides give somewhat greater lowering than the chlorides and the iodides even greater lowering than the bromides.

As far as comparisons can be made, it seems that the nitrates produce about the same lowerings as the corresponding chlorides with an equal number of molecules of water of crystallization and, therefore, somewhat less than the corresponding bromides and iodides.

The quarternary chlorides of aluminium and iron cannot be compared, at present, with respect to their freezing-point lowering, with the corresponding bromides and iodides, because the latter have not yet been investigated, but they will be studied as soon as possible.

A comparison of the lowerings produced by the chlorides of

iron and aluminium, containing 6 molecules of crystal water, with the nitrates of the same metals which have a larger amount of water of crystallization, will show a somewhat greater lowering, at the same concentrations, produced by the nitrates.

Thus, *relations between the lowering of the freezing-point of water produced by salts and their water of crystallization, comes out on every hand, whether we compare the salts of a given acid with different metals, or the salts of the same metal with different acids.*

This line of evidence, together with several others already pointed out in earlier papers, confirms us in the belief of the correctness of the theory, advanced by one of us,[1] to account for the abnormally great depressions of the freezing-point of water, produced by electrolytes, *viz., that in solution the dissolved substance is in combination with a part of the solvent; the amount of the solvent held in combination by the dissolved substance being a function of the concentration of the solution; in general, increasing with increase in concentration.*

In earlier papers[2] attempts were made to calculate the approximate composition of the hydrates formed by a number of substances at different dilutions. As was pointed out, this is not an easy matter for several reasons, especially on account of the difficulty of determining the dissociation in the more concentrated solutions. A number of the substances already studied undergo marked hydrolysis in dilute solution, so that it is impossible to determine the value of $\mu\infty$ in the usual way, by the conductivity method. A method, which would probably give $\mu\infty$ in such cases, that would not be very widely removed from the true value, was worked out and employed by Jones and Getman.[3] It consists in combining the freezing-point and conductivity methods as follows: The dissociation for two or three dilute solutions of a substance was determined by the freezing-point method and their conductivities also measured. Knowing α and μ_v, $\mu\infty$ could be calculated at once. This method was proposed and applied, however, only tenta-

[1] Jones: THIS JOURNAL, **23**, 89 (1900).
[2] *Ibid.*, **31**, 303 (1904). Z. physik. Chem., **49**, 385 (1904).
[3] THIS JOURNAL, **31**, 303 (1904). Z. physik. Chem., **49**, 385 (1904).

tively. It was pointed out that it is merely an approximation, but, with the data then at our disposal, it was the sole means of obtaining any idea as to the magnitude of the hydration for a given substance and of the change in the complexity of the hydrates with change in concentration.

It must also be repeated that the conductivity method is not an accurate measure of dissociation in concentrated solutions, yet it probably gives values of the right order of magnitude and, at present, is the best that can be done in such cases.

The Present Investigation.

The object of the present investigation is to calculate, as closely as possible, the composition of the hydrates formed by a number of electrolytes, over as wide range of concentration as work could be extended. In order to accomplish this the following data had to be secured: The lowering of the freezing-point, produced by the various solutions, had to be determined and the molecular lowering calculated from the observed value.

The conductivities of the solutions at 0° must be measured and also the value of $\mu\infty$ by the conductivity method, wherever this could be done. The object of these measurements was to ascertain, as closely as possible, the dissociation of the solution in question, in order that the theoretical lowering produced by the substance, if there was no hydration, could be calculated.

The specific gravities of all of the solutions must also be measured. The object of this was to determine the actual amount of water in a liter of the solution. The difference between the amount of water in a liter of a dilute solution and 1000 grams is small, but, in concentrated solutions, the difference may, of course, be very large.

Calculation of the Composition of the Hydrates.

Given the above data, the calculation of the amount of water in combination with the dissolved substance is simple. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present

in 1 liter of the solution. This gives the true molecular lowering, produced by the substance at the dilution in question, if there were 1000 grams of water present.

The calculated molecular lowering can now be compared directly with the corrected, observed, molecular lowering. If there was no hydration these two values would be equal. The magnitude of the hydration is obtained as follows:

The calculated molecular lowering is divided by the corrected molecular lowering found. This ratio, multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present was dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams is the quantity that is in combination with the dissolved substance, under the conditions that obtain in the solution in question.

For a number of reasons everything is referred to 1000 grams of the solvent. The theoretical freezing-point constant is calculated for 1000 grams of the solvent and, by calculating the depression found for the same amount of the solvent, the two sets of results are comparable. Further, by referring everything to a constant amount of the solvent, the various results can be compared directly with one another.

If we know the number of grams of water that have combined with the dissolved substance, the number of gram-molecules of water that have entered into combination is obtained by dividing the above value by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water in combination with 1 molecule of the dissolved substance, when the amount of substance present in a liter of the solution is dissolved in 1000 grams of water.

The Results.

In order to calculate the composition of the hydrates formed by any given substance, at different dilutions, it is necessary to have the following values:

The lowering of the freezing-point produced by the dissolved substance.

The conductivity of the solution as an approximate measure of its dissociation.

The specific gravities of the solutions, in order to calculate the difference between 1000 grams of water and the amount contained in a liter of the solution.

Some of the above data were already available for the following substances. However, in many cases only a part of the data had been secured and this we have supplemented wherever necessary.

The compositions of the hydrates, formed by the following substances, are calculated as closely as seems to be possible, at present :

Calcium chloride, calcium bromide, strontium bromide, barium bromide, magnesium chloride and bromide, manganese chloride and nitrate, cobalt chloride and nitrate, nickel chloride and nitrate, copper chloride and nitrate and sulphuric acid.

In the various tables of data the symbols have the following significance :

In the tables of freezing-point measurements m is the concentration in terms of gram-molecules per liter ; Δ the observed freezing-point lowering, corrected for the separation of ice ; $\frac{\Delta}{m}$ the molecular lowering of the freezing-point.

In the conductivity tables the symbols have the usual significance, v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte, α is the approximate dissociation.

In the specific gravity tables m is the concentration, $W_{Sol.}$ is the weight of 25 cc. of the solution, W_{Salt} is the weight of the salt contained in 25 cc. of the solution, W_{H_2O} is the weight of water contained in 25 cc. of the solution. The percentage correction is the correction that must be applied to the freezing-point lowering, in order to refer it to 1000 grams of solvent, instead of the amount of water that is present in a liter of the solution in question.

The symbols in the hydrate tables have the following significance : m is the concentration in terms of gram-molecules per liter, α the approximate dissociation of the solution, L the theoretical molecular lowering of the freezing-point referred to

1000 grams of the solvent, $\frac{\Delta}{m}$ the molecular lowering found experimentally, L′ the molecular lowering, m' the number of gram-molecules of water in combination, both being referred to 1000 grams of water. H the number of molecules of water in combination with 1 molecule of the salt, at the concentration in question, if a liter of the solution, at that concentration, contained 1000 grams of water.

In order to ascertain the number of molecules of water actually in combination with 1 molecule of the dissolved substance, at the concentration given, it is only necessary to divide the value of M, for that concentration, by the concentration expressed in terms of a gram-molecular weight in 1000 grams of the solvent. The difference between the values of H found by these two methods is generally quite negligible, being smaller than experimental errors. It becomes appreciable only when the "correction" per cent is large, *i. e.*, in very concentrated solutions.

Calcium Chloride.

The data for calcium chloride are given in Tables I. to IV. The freezing-point lowerings had already[1] been determined and

Table I.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.102	0°.505	4.98
0.153	0°.752	4.91
0.204	1°.012	4.96
0.255	1°.267	4.97
0.306	1°.537	5.02
0.408	2°.104	5.16
0.510	2°.681	5.26
0.612	3°.348	5.47
1.000	6°.345	6.345
1.500	11°.296	7.531
2.000	17°.867	8.934
1.949	17°.710	9.03
2.274	23°.000	10.11
2.598	29°.000	11.16
2.923	37°.400	12.79
3.248	46°.500	14.32

[1] Jones and Getman : Z. physik. Chem., 49, 442 (1904).

Table II.—Conductivity Measurements.

$\mu\infty$ 0° = 138.

v.	μ_v 0°.	α.
9.80	105.7	76.6
6.54	102.9	74.6
4.90	98.40	71.3
3.92	96.92	70.2
3.27	89.61	64.9
2.45	89.10	64.6
1.96	88.24	63.9
1.63	84.25	61.1
1.00	71.15	51.6
0.67	62.06	45.0
0.50	54.05	39.1
0.43	48.83	35.4
0.38	44.44	30.8
0.34	39.55	28.7
0.31	35.88	26.0

Table III.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.102	25.2408	0.2831	24.9577	0.17
0.153	25.3166	0.4246	24.8920	0.43
0.204	25.4635	0.5661	24.8974	0.41
0.255	25.6176	0.7076	24.9100	0.36
0.306	25.7050	0.8492	24.8558	0.58
0.408	26.0032	1.1322	24.8710	0.52
0.510	26.2300	1.4152	24.8148	0.74
0.612	26.5403	1.6983	24.8420	0.63
1.000	27.3656	2.7750	24.5906	1.64
1.500	28.4996	4.1625	24.3371	2.65
2.000	29.5984	5.5500	24.0484	3.81
2.274	29.8363	6.2992	23.5371	5.85
2.598	30.4502	7.2150	23.2352	7.05
2.923	31.1440	8.0780	23.0660	7.74
3.248	31.7437	9.0188	22.7249	9.10

Table IV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.102	0.766	4.71	4.98	4.97	3.02	29.6
0.153	0.746	4.64	4.91	4.89	2.84	18.6
0.204	0.713	4.51	4.96	4.94	4.84	23.7
0.255	0.702	4.47	4.97	4.95	5.39	21.2
0.306	0.649	4.27	5.02	4.99	8.02	26.2
0.408	0.646	4.26	5.16	5.13	9.42	23.1
0.510	0.639	4.24	5.26	5.22	10.41	20.4
0.612	0.611	4.13	5.47	5.44	14.40	23.5
1.000	0.516	3.78	6.345	6.24	22.80	22.8
1.500	0.450	3.55	7.53	7.33	28.65	19.1
2.000	0.391	3.31	8.934	8.59	34.15	17.1
2.274	0.354	3.08	10.11	9.52	37.58	16.5
2.598	0.308	3.01	11.16	10.37	39.43	15.2
2.923	0.287	2.93	12.79	11.80	41.76	14.2
3.248	0.260	2.83	14.32	13.02	42.81	13.2

a portion of the conductivity measurements made. The data necessary for calculating the hydration in dilute solutions was partly lacking and this was obtained.

The value of $\mu\infty$ for calcium chloride and for a number of the other salts used in this work, was determined by Mr. West, to whom we wish to express our thanks.

From column m it will be seen that the amount of water that has entered into combination increases with the concentration of the solution. This is just what we should expect from the law of mass action. The larger the amount of the salt present, the greater the amount of water that would be held in combination. The slight increase in the amount of water combined as we pass from 0.153 normal to 0.102 normal is to be noted, because a similar phenomenon occurs in other cases.

If we turn our attention to the number of molecules of water combined with 1 molecule of the dissolved substance, we shall see that this increases from the most concentrated solution to about half-normal and then, with considerable fluctuation, does not change in any decided manner. The number of molecules of water in combination with 1 molecule of the dissolved substance is really of less interest and importance than the *total amount* of water held in combination by the dissolved

substance, the latter has, therefore, been plotted in the curve (Fig. V.), against the concentrations as abscissae. The curve

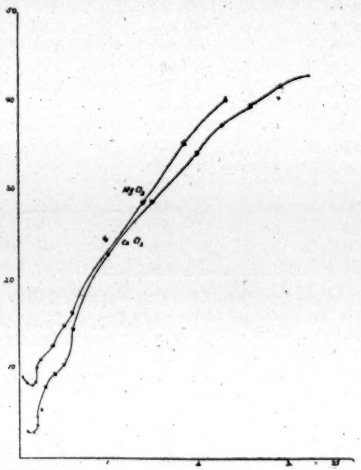


Fig. V.

shows, at a glance, that the amount of water held in combination increases, and fairly regularly, with the concentration.

Calcium Bromide.

What has been said in reference to calcium chloride holds largely for the bromide. Such data as were lacking were obtained, especially for dilute solutions, in order that the approximate magnitude of the hydration in such solutions could be calculated. The value of $\mu\infty$ at 0°, for calcium bromide, was also obtained directly, by the conductivity method.

The total amount of water held in combination increases with the concentration (see Fig. VII., p. 558). The bromide combines with a little more water than the chloride, at the same concentrations.

Table V.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0435	0°.228	5.24
0.0871	0°.445	5.11
0.1306	0°.664	5.07
0.1742	0°.904	5.18
0.2613	1°.368	5.23
0.3484	1°.847	5.30
0.4355	2°.397	5.50
0.5226	2°.949	5.60
0.452	2°.340	5.18
0.903	6°.200	5.86
1.506	13°.100	8.69
1.807	17°.500	9.07
2.409	30°.500	12.66
3.011	47°.000	15.61

Table VI.—Conductivity Measurements.

$\mu\infty$ 0° = 123.7.

v.	μ_v 0°.	α.
22.98	107.42	86.8
11.48	100.53	81.3
7.66	98.29	79.5
5.74	94.53	76.4
3.83	93.19	75.3
2.87	89.44	72.3
2.30	87.59	70.8
1.91	85.86	69.4
1.11	80.9	65.4
0.66	68.3	55.2
0.55	61.7	49.9
0.415	50.14	40.5
0.332	39.68	32.1

Table VII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	W_{Salt}.	W_{H_2O}.	Correction. Per cent.
0.0435	25.1605	0.2177	24.9428	0.23
0.0871	25.3421	0.4355	24.9066	0.37
0.1306	25.5154	0.6530	24.8624	0.55
0.1742	25.7263	0.8710	24.8553	0.58
0.2613	26.0433	1.3065	24.7368	1.05
0.3484	26.3743	1.7420	24.6323	1.47
0.4355	26.7319	2.1772	24.5547	1.78
0.5226	27.0749	2.6130	24.4619	2.15
0.9030	28.7128	4.5150	24.1978	3.21
1.5060	31.1185	7.5300	23.5885	5.65
1.8070	32.3080	9.0350	23.2730	6.91
2.4090	34.6443	12.0450	22.5993	9.60
3.0110	37.0233	15.0550	21.9683	12.13

Table VIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.0435	0.868	5.13	5.24	5.23	1.06	24.4
0.0871	0.813	4.88	5.11	5.09	2.29	26.3
0.1306	0.795	4.82	5.07	5.04	2.43	18.5
0.1742	0.764	4.70	5.18	4.88	2.05	11.7
0.2613	0.753	4.66	5.23	5.18	5.58	21.3
0.3484	0.723	4.55	5.30	5.22	7.13	20.5
0.4355	0.708	4.49	5.50	5.40	9.36	21.3
0.5226	0.694	4.44	5.60	5.48	10.54	20.2
0.903	0.654	4.29	5.86	5.67	13.52	15.0
1.506	0.552	3.91	8.69	8.20	29.06	12.7
1.807	0.499	3.72	9.07	8.64	31.61	17.5
2.409	0.405	3.37	12.66	11.44	39.19	16.2
3.011	0.321	3.05	15.61	13.72	43.21	14.3

Strontium Bromide.

Although the freezing-point lowering had been determined[1]

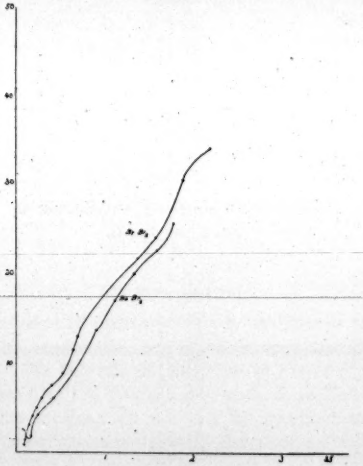


Fig. VI.

[1] Jones and Getman: Z. physik. Chem., 49, 405.

over the entire range of concentration that could be brought within this investigation, conductivity and specific gravity data had to be obtained. The value of $\mu\infty$ at 0° for strontium bromide was determined for us by Mr. West and is given below.

The results are of the same general character as those obtained with calcium chloride and bromide. The amount of water held in combination increases with the concentration, from the most dilute to the most concentrated solution and about the same quantity of water is combined as with the calcium salts, at the same concentration (see Fig. VIII., p. 563).

Table IX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.053	0°.262	5.04
0.103	0°.503	4.88
0.155	0°.773	4.98
0.207	1°.035	5.00
0.259	1°.308	5.05
0.310	1°.592	5.13
0.414	2°.147	5.19
0.517	2°.741	5.30
0.621	3°.447	5.55
0.626	3°.502	5.59
1.565	12°.520	8.00
1.878	16°.500	8.78
2.191	22°.000	10.04

Table X.—Conductivity Measurements.

$\mu\infty$ 0° = 129.6.

v.	μ_v 0°.	α.
19.23	107.4	82.9
9.71	102.1	78.8
6.45	97.65	75.3
4.83	95.07	73.4
3.86	94.55	73.0
3.22	92.84	71.6
2.42	89.43	68.9
1.92	87.61	67.5
1.61	84.52	65.1
0.63	67.83	52.3
0.53	61.10	47.1
0.45	55.70	43.0

Table XI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.052	25.2438	0.3219	24.9219	0.31
0.103	25.5540	0.6376	24.9164	0.33
0.155	25.7882	0.9657	24.8225	0.71
0.207	26.0497	1.2872	24.7625	0.91
0.259	26.3649	1.6090	24.7559	0.98
0.310	26.6038	1.9201	24.6837	1.26
0.414	27.1646	2.5602	24.6044	1.58
0.517	27.6870	3.2002	24.4868	2.05
0.621	28.2420	3.8440	24.3980	2.40
0.626	28.1763	4.0734	24.1029	3.59
1.565	32.8955	9.7144	23.1811	7.28
1.878	34.4696	11.6325	22.8371	8.65
2.191	36.0403	13.5493	22.4910	10.04

Table XII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.052	0.829	4.94	5.04	5.02	0.886	17.0
0.103	0.788	4.73	4.88	4.86	1.488	14.4
0.155	0.753	4.66	4.98	4.94	3.15	20.3
0.207	0.734	4.59	5.00	4.95	4.04	19.5
0.259	0.730	4.57	5.05	5.00	4.78	18.4
0.310	0.716	4.52	5.13	5.07	6.04	19.5
0.414	0.689	4.42	5.19	5.11	7.50	18.1
0.517	0.675	4.37	5.30	5.19	8.78	17.0
0.621	0.651	4.28	5.55	5.42	11.69	18.8
1.565	0.523	3.81	8.00	6.70	23.96	15.3
1.8778	0.471	3.61	8.78	8.02	30.55	16.2
2.191	0.430	3.46	10.04	9.03	34.16	15.6

Barium Bromide.

The freezing-point measurements in the case of barium bromide had also been made,[1] but much of the other data had to be secured. We determined the value of $\mu\infty$ at 0° by the direct application of the conductivity method, at high dilutions.

The results obtained do not call for special discussion, because they are of the same general character as those already considered. The amount of the solvent held in combination

[1] Jones and Getman: Z. physik. Chem., 49, 407 (1904).

by barium bromide is about the same, at comparable concentrations, as for the other halides of the calcium group, after the first dilution, it increases with the concentration. The results are plotted in a curve, Fig. VI., p. 551.

Table XIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.10	0°.506	5.06
0.15	0°.737	4.91
0.20	1°.001	5.00
0.40	2°.039	5.09
0.50	2°.591	5.18
0.4516	2°.310	5.11
0.6774	3°.890	5.74
0.9032	7°.300	5.87
1.1290	7°.050	6.24
1.3548	9°.020	6.66
1.5806	11°.260	7.12
1.8064	13°.860	7.67
2.258	19°.030	8.43

Table XIV.—Conductivity Measurements.

$\mu\infty$ 0° = 136.9.

v.	μ_v 0°.	α.
10.00	108.5	79.3
6.67	106.3	77.7
4.00	101.0	73.8
2.50	97.60	71.3
2.00	94.23	68.8
1.47	89.40	65.3
1.11	88.76	64.8
0.88	83.60	61.1
0.74	79.94	58.4
0.63	76.10	55.6
0.55	69.70	50.9
0.44	56.20	41.1

Table XV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	25.6280	0.7433	24.8847	0.46
0.15	25.9603	1.1149	24.8454	0.62
0.25	26.6335	1.8581	24.7754	0.90
0.40	27.5884	2.9730	24.6154	1.14
0.50	28.2854	3.7163	24.5691	1.72
0.6774	29.3522	5.0058	24.3464	2.61
0.9032	30.7874	6.6915	24.0959	3.62
1.1290	32.1553	8.4016	23.7537	4.99
1.3548	33.6259	10.0373	23.5886	5.65
1.5806	35.0292	11.7473	23.2819	6.87
1.8064	36.4501	13.4574	22.9927	8.03
2.258	39.2792	16.8031	22.4761	10.09

Table XVI.—Hydrates.

m.	*a.*	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.10	0.793	4.81	5.06	5.04	2.54	25.4
0.15	0.777	4.75	4.91	4.88	1.48	9.9
0.25	0.738	4.60	5.00	4.96	4.03	16.1
0.40	0.713	4.52	5.09	5.03	5.63	14.1
0.50	0.688	4.42	5.18	5.09	6.22	12.5
0.6774	0.653	4.29	5.74	5.59	12.92	19.1
0.9032	0.648	4.27	5.87	5.66	13.64	15.1
1.1290	0.611	4.13	6.24	5.93	16.88	14.9
1.3548	0.584	4.03	6.66	6.28	19.90	14.7
1.5806	0.556	3.93	7.12	6.63	22.62	14.3
1.8064	0.509	3.75	7.67	7.06	26.05	14.4
2.258	0.411	3.39	8.43	7.58	30.71	13.6

Magnesium Chloride.

The freezing-point lowerings produced by magnesium chloride were measured by Jones and Getman.[1] The remaining data, especially for the dilute solutions, we have secured.

Magnesium chloride has greater power to combine with water than any of the halides of the calcium group. The difference is especially marked in the dilute solutions. Notwithstanding this fact, we see that the amount of water held in combination by the magnesium salt increases regularly with

[1] Z. physik. Chem., 49, 411 (1904).

increase in concentration (see Fig. V., p. 549). There is here also a slight exception presented by the first two solutions. It is worth noting that the amount of water combined with 1 molecule of the dissolved substances increases from the most dilute to the most concentrated solution.

Table XVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0508	0°.280	5.51
0.1016	0°.537	5.28
0.1525	0°.771	5.06
0.2033	1°.058	5.20
0.2541	1°.335	5.25
0.3801	2°.015	5.30
0.5082	2°.762	5.43
0.6099	3°.472	5.69
0.464	2°.482	5.35
0.927	6°.140	6.62
1.391	10°.820	7.78
1.854	17°.380	9.38
2.318	27°.000	11.60

Table XVIII.—Conductivity Measurements.

$\mu\infty$ 0° = 120.0.

v.	μ_v 0°.	α.
19.69	88.64	73.9
9.84	83.30	69.4
6.56	79.11	65.9
4.87	76.28	63.6
3.94	74.84	62.4
2.63	70.51	58.8
1.97	66.59	55.5
1.64	64.39	53.8
1.08	63.43	52.9
0.70	52.65	43.9
0.54	45.70	38.1
0.43	36.67	30.6

Table XIX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0508	25.0818	0.1210	24.9608	0.16
0.1016	25.1641	0.2420	24.9221	0.31
0.1525	25.2596	0.3629	24.8967	0.41
0.2033	25.3275	0.4839	24.8436	0.62
0.2541	25.4230	0.6050	24.8180	0.73
0.3801	25.6426	0.9074	24.7352	1.06
0.5082	25.8768	1.2098	24.6670	1.33
0.6099	26.0392	1.4520	24.5872	1.65
0.927	26.7206	2.2134	24.5072	1.97
1.391	27.5109	3.3082	24.2027	3.19
1.854	28.3128	4.4030	23.9098	4.36
2.318	29.0447	5.5216	23.5231	5.91
2.782	29.8178	6.6164	23.2014	7.19

Table XX.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.1016	0.694	4.44	5.28	5.26	8.41	82.7
0.1525	0.659	4.31	5.06	5.04	8.05	52.1
0.2033	0.636	4.23	5.20	5.17	10.10	49.7
0.2541	0.624	4.18	5.25	5.21	10.99	43.3
0.3801	0.588	4.05	5.30	5.24	12.62	33.2
0.5082	0.555	3.92	5.43	5.36	14.93	29.4
0.6099	0.538	3.86	5.69	5.60	17.26	28.3
0.927	0.529	3.83	6.62	6.50	23.93	25.8
1.391	0.439	3.49	7.78	7.53	29.81	21.4
1.854	0.381	3.28	9.38	8.97	35.29	19.0
2.318	0.306	3.00	11.60	10.91	40.28	17.4

Magnesium Bromide.

The bromide of magnesium, like the chloride, had already been studied by Jones and Getman.[1] They were interested especially in the magnitude of the hydration in concentrated solutions; much of the data necessary to calculate the approxi-

[1] Z. physik. Chem., 49, 412 (1904).

mate composition of the hydrates, in dilute solution, we had to secure.

The results for magnesium bromide are very similar to those for magnesium chloride. The amount of water held in combination is larger than in the case of any bromide of the calcium group. We notice here, also, a decrease in the value of m for the first two solutions, then a regular increase with the concentration (see Fig. VII.).

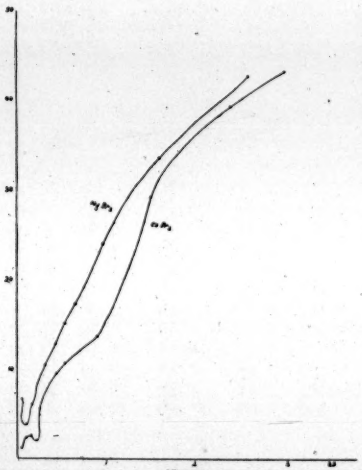


Fig. VII.

Here, again, the number of molecules of water combined with 1 molecule of the salt, increases from the most dilute to the most concentrated solution.

Table XXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0517	0°.277	5.36
0.103	0°.531	5.14
0.155	0°.801	5.17
0.207	1°.088	5.26
0.310	1°.690	5.45
0.414	2°.347	5.67
0.517	3°.022	5.84
0.321	1°.691	5.27
0.642	3°.921	6.17
0.964	6°.850	7.11
1.610	15°.200	9.44
2.571	37°.500	14.60

Table XXII.—Conductivity Measurements.

$\mu\infty$ 0° = 122.8.

v.	μ_v 0°.	α.
19.23	100.3	81.7
9.71	94.55	77.0
6.45	90.62	73.8
4.83	88.49	72.6
3.22	82.66	67.3
3.11	81.86	66.7
2.42	79.90	65.1
1.92	77.04	62.7
1.56	75.56	61.5
1.03	68.31	55.6
0.62	54.63	44.5
0.39	37.28	30.4

Table XXIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0517	25.1526	0.2379	24.9147	0.34
0.103	25.3540	0.4758	24.8782	0.49
0.155	25.5990	0.7138	24.8852	0.46
0.207	25.7553	0.9518	24.8035	0.79
0.310	26.1085	1.4275	24.6810	1.27
0.321	26.1549	1.4736	24.6813	1.27
0.414	26.5794	1.9070	24.6724	1.74
0.517	26.9461	2.3792	24.5669	1.73
0.642	27.3491	2.9472	24.4019	2.39
0.964	28.4985	4.4208	24.0777	3.69
1.610	30.7930	7.3680	23.4250	6.30
2.571	34.1739	11.9730	22.2009	11.19
3.214	36.1581	14.7360	21.4221	14.31

Table XXIV.—Hydrates.

m.	*a.*	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.103	0.770	4.75	5.14	5.11	3.81	38.0
0.155	0.738	4.60	5.17	5.15	5.93	38.3
0.207	0.726	4.56	5.26	5.22	7.02	33.9
0.310	0.673	4.36	5.45	5.38	10.53	33.97
0.414	0.651	4.28	5.67	5.57	12.87	31.1
0.517	0.627	4.19	5.84	5.74	15.00	29.0
0.642	0.615	4.15	6.17	6.02	17.26	26.9
0.964	0.556	3.93	7.11	6.85	23.68	25.6
1.610	0.445	3.52	9.44	8.85	33.46	20.8
2.571	0.304	2.99	14.60	12.97	42.80	16.6

Manganese Chloride.

The substances dealt with in the remainder of this paper were studied by Jones and Getman,[1] in their earlier work. At that time the evidence for the existence of hydrates in solution was not recognized as clearly as it is to-day and no effort was then made to calculate the composition of the hydrates formed by these compounds.

We have taken the earlier data as far as they bear on the problem in hand and have supplemented them, wherever neces-

[1] THIS JOURNAL, 31, 303 (1904).

sary, in order to calculate the approximate composition of the hydrates formed by these various substances, at different concentrations. This necessitated many new freezing-point determinations; in all cases new conductivity measurements at

Table XXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.053	0°.255	4.81
0.106	0°.508	4.79
0.133	0°.639	4.80
0.266	1°.259	4.73
0.400	2°.004	5.01
0.532	2°.790	5.24
0.796	4°.247	5.34
0.902	4°.825	5.36
1.061	5°.965	5.62
1.500	11°.100	6.66
2.000	16°.500	8.25
2.500	24°.000	9.60
3.000	31°.000	10.33
3.500	40°.000	11.43
4.000	48°.500	12.13

Table XXVI.—Conductivity Measurements.

$\mu\infty$ 0° = 123.

v.	μ_v 0°.	α.
18.87	88.67	72.0
9.43	81.81	67.0
7.51	79.85	65.0
3.76	73.49	60.0
1.88	65.16	53.0
1.26	57.32	47.0
0.94	51.44	42.0
0.66	43.35	34.0
0.50	34.82	28.0
0.40	26.38	21.0
0.33	19.67	16.0
0.29	14.04	11.0
0.25	9.82	8.0

Table XXVII.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.133	25.2679	0.4186	24.8593	0.56
0.266	25.6125	0.8372	24.7753	0.90
0.400	25.9469	1.2590	24.6879	1.25
0.532	26.2766	1.6745	24.6021	1.59
0.796	26.9452	2.5154	24.4298	2.28
0.902	27.1870	2.8390	24.3480	2.61
1.061	27.6633	3.3394	24.3239	2.70
1.500	28.7249	4.7213	24.0036	3.98
2.000	29.8916	6.2950	23.5966	5.62
2.500	31.0396	7.8688	23.1708	7.32
3.000	32.0541	9.4425	22.6116	9.55
3.500	33.2645	11.0138	22.2507	11.00
4.000	34.5927	12.5900	22.0027	11.99

Table XXVIII.—Hydrates.

m.	*α*.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.133	0.65	4.28	4.80	4.77	5.7	42.8
0.266	0.60	4.09	4.73	4.69	7.1	26.7
0.532	0.53	3.83	5.24	5.16	15.4	28.9
0.796	0.47	3.61	5.34	5.22	17.13	21.5
1.061	0.42	3.42	5.62	5.47	20.8	19.6
1.500	0.34	3.12	6.66	6.40	28.9	19.3
2.000	0.28	2.90	8.25	7.79	34.9	17.5
2.500	0.21	2.64	9.60	8.90	39.1	15.6
3.000	0.16	2.46	10.33	9.34	40.9	13.6
3.500	0.11	2.27	11.43	10.18	43.2	12.3
4.000	0.08	2.16	12.13	10.68	44.3	11.1

0° and the specific gravities of all of the solutions had to be ascertained.

An examination of Table XXVIII. will show that manganese chloride resembles the chlorides already studied, in that the power to combine with water is great and increases regularly, from the most dilute to the most concentrated solution. This is also shown by the curve for this substance in Fig. VIII.

The number of molecules of water combined with 1 molecule

of the salt increases from the most concentrated to the most dilute solution. We have already met with other substances

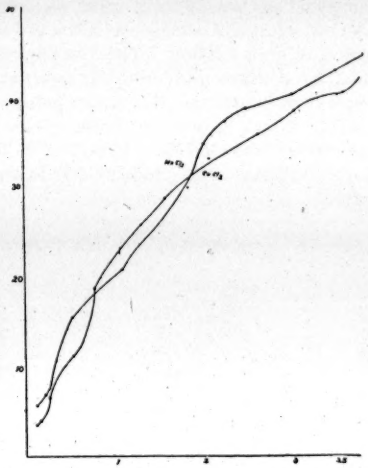


Fig. VIII.

where this is the case, notably magnesium chloride and bromide.

Manganese Nitrate.

The results formerly obtained by Jones and Getman[1] for manganese nitrate were somewhat out of keeping for a salt with 6 molecules of water of crystallization. The freezing-point lowerings, produced by this substance, were too small. Suspecting that there must have been some error, as far as this substance is concerned, we repeated the work. The following results were obtained :

From Table XXIX. it will be seen that manganese nitrate gives just about the same lowering of the freezing-point as other salts with 6 molecules of water of crystallization and

[1] THIS JOURNAL, 31, 313 (1904).

really falls right in line with the relation that has been shown to hold in such a large number of cases.

In order to avoid any possibility of error, we prepared a second, entirely new, solution of manganese nitrate and made a fresh standardization of this solution. The freezing-point lowerings, produced by solutions made from this newly standardized solution, were then determined, the results being recorded in Table XXXIII. It will be seen that these agree satisfactorily with the results in Table XXIX. The error in the original work with this substance was probably due to a mistake in standardization.

Table XXIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.27	1°.39	5.15
0.54	2°.98	5.52
1.05	6°.75	6.43
1.59	12°.00	7.55
2.61	27°.50	10.54
3.15	38°.50	12.22

Table XXX.—Conductivity Measurements.

$\mu\infty$ 0° = 112.

v.	μ_v.	α.
3.70	80.62	72.0
1.85	71.37	63.7
0.95	58.48	52.2
0.63	48.61	43.4
0.38	27.37	24.4
0.32	20.02	17.9

Table XXXI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.27	25.8667	1.2087	24.6580	1.37
0.54	26.7980	2.4175	24.3805	2.48
1.05	28.4612	4.8350	23.6262	5.50
1.59	30.2003	7.1184	23.0819	7.67
2.61	33.4161	11.6850	21.7311	13.08
3.15	35.0516	14.1026	20.9490	16.20

Table XXXII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.09	0.824	4.93	5.11	5.09	1.75	19.4
0.18	0.766	4.71	4.90	4.86	1.72	9.53
0.27	0.720	4.54	5.15	5.08	5.91	21.87
0.54	0.637	4.23	5.52	5.38	11.87	21.99
1.05	0.522	3.80	6.43	6.08	20.83	19.84
1.59	0.434	3.47	7.55	6.97	27.90	17.55
2.61	0.244	2.77	10.54	10.04	40.23	15.41
3.15	0.179	2.53	12.22	10.24	41.82	13.28

Table XXXIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.09	0°.46	5.11
0.18	0°.88	4.90
0.27	1°.43	5.30
0.54	3°.07	5.69
1.05	6°.80	6.47
1.59	11°.80	7.42
2.61	27°.00	10.35
3.105	38°.00	12.24

Cobalt Chloride.

Only a very small number of the results for cobalt chloride had been obtained by Jones and Getman.[1] This applies also to the freezing-point lowerings, since only those produced by dilute solutions had been measured. The same holds for the conductivity measurements; all of the specific gravity determinations have been made by us.

The results are just what we should expect. Cobalt chloride crystallizes with 6 molecules of water and, like the other chlorides with this amount of crystal water, has large hydrating power. The amount of water combined with the salt increases, regularly, with the concentration of the solution, as is shown by the curve for this substance in Fig. IX.

[1] THIS JOURNAL, 31, 322 (1904).

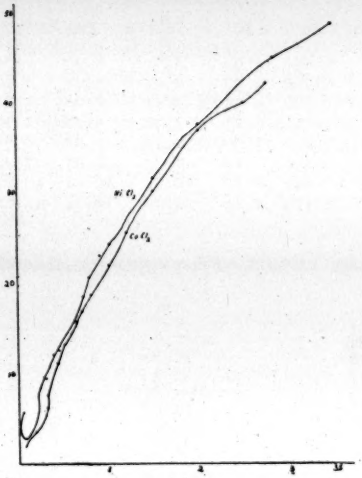


Fig. IX.

Table XXXIV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0639	0°.325	5.09
0.1279	0°.631	4.94
0.1918	0°.946	4.93
0.3197	1°.640	5.13
0.4475	2°.427	5.43
0.5114	2°.817	5.51
0.6393	3°.658	5.72
0.700	4°.000	5.71
0.800	4°.700	5.88
0.900	5°.420	6.00
1.000	6°.240	6.24
1.500	11°.520	7.68
2.000	19°.000	8.50
2.500	27°.500	11.00
2.760	33°.500	12.14

Table XXXV.—Conductivity Measurements.

$\mu\infty$ 0° = 117.

v.	μ_v 0°.	*α.*
15.65	95.93	82.0
7.82	88.42	75.6
5.21	86.36	73.9
3.12	79.50	67.9
2.23	74.45	63.6
1.95	71.53	61.1
1.57	67.94	58.1
1.43	64.38	55.0
1.25	61.48	52.6
1.11	58.93	50.3
1.00	57.25	48.9
0.667	47.34	40.5
0.50	37.93	32.4
0.40	29.79	25.5
0.362	26.13	22.3

Table XXXVI.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0693	25.1826	0.2077	24.9749	0.10
0.1279	25.3374	0.4154	24.9220	0.31
0.1918	25.5253	0.6229	24.9024	0.43
0.3197	25.8939	1.0382	24.8557	0.58
0.4475	26.2241	1.4533	24.7708	0.92
0.5114	26.4026	1.8583	24.5443	1.82
0.6393	26.7464	2.0761	24.6703	1.32
0.70	26.9935	2.2732	24.7203	1.12
0.80	27.2334	2.5980	24.6354	1.46
0.90	27.4400	2.9227	24.5173	1.93
1.00	27.7211	3.2475	24.4736	2.11
1.50	29.1942	4.8712	24.3230	2.71
2.00	30.4874	6.4950	23.9924	4.03
2.50	31.8077	8.1187	23.6890	5.24
2.76	32.5739	9.1931	23.3808	6.48

Table XXXVII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.0639	0.820	4.91	5.09	5.08	1.86	29.1
0.1279	0.756	4.67	4.94	4.92	2.71	21.2
0.1918	0.739	4.61	4.93	4.91	3.42	17.9
0.3197	0.679	4.39	5.13	5.10	7.73	21.1
0.4475	0.636	4.23	5.43	5.38	11.42	25.5
0.5114	0.611	4.13	5.51	5.41	13.14	25.7
0.6393	0.581	4.02	5.72	5.64	15.96	25.1
0.700	0.550	3.91	5.71	5.64	17.04	24.3
0.800	0.526	3.82	5.88	5.80	18.96	23.8
0.900	0.503	3.73	6.00	5.88	20.31	22.6
1.000	0.489	3.68	6.24	6.11	22.09	22.1
1.500	0.405	3.37	7.68	7.47	30.48	20.3
2.000	0.324	3.07	9.50	9.46	37.53	18.8
2.500	0.255	2.81	11.00	10.42	40.57	16.2
2.760	0.223	2.69	12.14	11.35	42.38	15.3

Cobalt Nitrate.

The nitrate of cobalt, like the chloride, crystallizes with 6 molecules of water of crystallization and we should expect hydrating power of the same order of magnitude. Such is the fact.

We worked with more concentrated solutions than had been previously used and supplemented the data obtained by Jones and Getman[1] for all of the solutions, so as to be able to calculate the composition of the hydrates at the various dilutions. The regular increase in the amount of water held in combination, with increase in the concentration of the solutions, is shown by the curve in Fig. X., p. 573.

Table XXXVIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0747	0°.352	4.72
0.1495	0°.685	4.58
0.2989	1°.388	4.65
0.4484	2°.198	4.87
0.7473	3°.935	5.28
1.0462	6°.025	5.76
1.3451	8°.418	6.26
1.4945	9°.811	6.55
2.000	17°.50	8.75
2.570	26°.50	10.60

[1] THIS JOURNAL, 31, 323 (1904).

Table XXXIX.—Conductivity Measurements.

$\mu\infty$ 0° = 117.6.

v.	μ_v 0°.	*α.*
13.39	87.68	74.6
6.69	81.80	69.5
3.35	75.00	63.8
2.23	69.46	57.1
1.35	62.43	53.1
0.95	54.60	46.4
0.74	48.17	41.0
0.67	45.47	38.7
0.50	36.09	30.7
0.389	26.59	22.6

Table XL.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0748	25.2794	0.3422	24.9372	0.25
0.1495	25.5716	0.6843	24.8873	0.45
0.2989	26.0667	1.3931	24.6736	1.31
0.4484	26.6273	2.0523	24.5750	1.70
0.7473	27.6680	3.4204	24.2476	3.01
1.0451	28.7815	4.7834	23.9981	4.01
1.3451	29.7903	6.1565	23.6338	5.47
1.4945	30.2888	6.8403	23.4485	6.21
2.00	32.1172	9.1540	22.9632	8.15
2.57	33.9705	11.7629	22.2076	11.17

Table XLI.—Hydrates.

m.	*α.*	[L.	$\frac{\Delta}{m}$.	L'.	M.	H.
0.0747	0.746	4.64	4.72	4.71	0.83	11.0
0.1495	0.695	4.45	4.58	4.56	1.34	9.0
0.2989	0.638	4.23	4.65	4.59	4.36	14.6
0.4484	0.571	3.98	4.87	4.79	9.39	20.95
0.7473	0.531	3.84	5.28	5.12	13.89	18.6
1.0462	0.464	3.59	5.76	5.53	19.49	18.6
1.3451	0.410	3.29	6.26	5.92	24.58	18.3
1.4945	0.387	3.10	6.55	6.14	27.51	18.4
2.000	0.307	3.00	8.75	8.04	37.31	18.6
2.570	0.226	2.70	10.60	9.42	39.63	15.4

Nickel Chloride.

The earlier work of Jones and Getman[1] had to do only with the more dilute solutions of nickel chloride. We have extended the earlier work from a concentration of only 0.743 N to 3.483 N.

The results with nickel nitrate are similar to those with cobalt chloride. The amount of water combined with the salt in solution increased regularly, from the most dilute to the most concentrated solution (see Fig. IX., p. 566). The number of molecules of water combined with 1 molecule of the salt increase, fairly regularly, from the most concentrated to the most dilute solution.

Table XLII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.037	0°.205	5.54
0.074	0°.380	5.11
0.149	0°.768	5.15
0.223	1°.170	5.25
0.297	1°.585	5.34
0.372	2°.032	5.46
0.446	2°.458	5.51
0.521	2°.945	5.65
0.743	4°.547	6.12
0.800	4°.880	6.10
0.900	5°.740	6.38
1.000	6°.580	6.58
1.500	11°.920	7.95
2.000	20°.000	10.00
2.500	31°.500	12.60
3.000	41°.500	16.60
3.483	53°.000	21.20

[1] THIS JOURNAL, 31, 317 (1904).

Table XLIII.—Conductivity Measurements.

$\mu\infty$ 0° = 120.7.

v.	μ_v 0°.	*α.*
27.0	103.2	85.5
13.5	97.0	80.4
6.7	88.64	73.4
4.48	85.50	70.8
3.38	82.52	68.4
2.68	77.9	64.5
2.24	77.2	64.0
1.92	75.2	62.3
1.35	70.23	58.2
1.25	61.87	51.2
1.11	59.19	49.0
1.00	58.23	48.2
0.667	46.85	38.8
0.50	38.59	32.0
0.40	29.88	24.8
0.33	22.85	18.9
0.287	16.92	14.0

Table XLIV.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.037	25.0835	0.1199	24.9636	0.15
0.074	25.1860	0.2398	24.9462	0.21
0.149	25.4198	0.4828	24.9370	0.25
0.223	25.6430	0.7225	24.9205	0.31
0.297	25.8450	0.9623	24.8827	0.47
0.372	26.0920	1.2028	24.8892	0.44
0.446	26.2954	1.4451	24.8503	0.60
0.521	26.4786	1.6881	24.7905	0.84
0.743	27.1588	2.4073	24.7515	0.95
0.800	27.3576	2.5920	24.7656	0.94
0.900	27.5953	2.9160	24.6793	1.28
1.000	27.9336	3.2400	24.6936	1.17
1.500	29.3731	4.8600	24.5131	1.55
2.000	30.7936	6.4800	24.3136	2.75
2.500	32.0714	8.1000	23.9714	4.11
3.000	33.5388	9.7200	23.8188	4.72
3.483	34.7943	11.2849	23.5094	5.96

Table XLV.—Hydrates.

m.	*a.*	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.074	0.804	4.85	5.11	5.10	2.73	36.9
0.149	0.734	4.60	5.15	5.14	5.83	39.2
0.223	0.708	4.49	5.25	5.23	7.86	35.2
0.297	0.684	4.40	5.34	5.31	9.41	31.7
0.372	0.645	4.26	5.46	5.43	11.97	32.2
0.446	0.640	4.24	5.51	5.48	12.57	28.2
0.521	0.623	4.16	5.65	5.60	14.28	27.4
0.743	0.582	4.04	6.12	6.06	18.52	24.9
0.800	0.512	3.76	6.10	6.04	20.97	26.2
0.900	0.490	3.68	6.38	6.31	23.15	25.7
1.00	0.482	3.65	6.58	6.50	24.36	24.4
1.500	0.388	3.30	7.95	7.83	32.14	21.4
2.00	0.320	3.05	10.00	9.73	38.08	19.0
2.500	0.248	2.78	12.60	12.18	42.88	17.2
3.00	0.189	2.56	16.60	15.82	46.57	15.6
3.483	0.140	2.38	21.20	19.85	48.90	13.8

Nickel Nitrate.

The freezing-point lowerings produced by solutions of nickel nitrate were studied pretty thoroughly by Jones and Getman. We have, however, been able to extend their investigations, even on freezing-point lowerings, to somewhat greater concentrations.

The hydrating power of nickel nitrate is of the same order as that of cobalt nitrate (see Fig. X., p. 573), just as we should expect, since it has the same number of molecules of water of crystallization.

Here, also, we notice that the number of molecules of water combined with 1 molecule of the salt, increases from the most concentrated to the most dilute solution.

[1] This Journal, 31, 318 (1904).

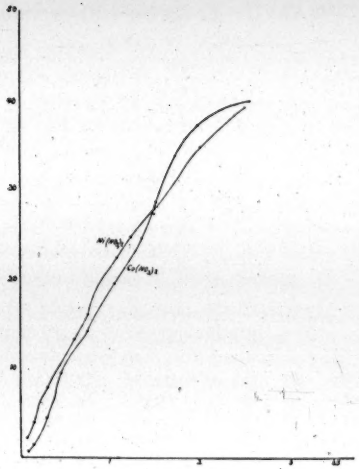


Fig. X.

Table XLVI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0761	0°.377	4.95
0.1522	0°.750	4.93
0.3044	1°.527	5.01
0.6088	3°.273	5.37
0.7610	4°.306	5.66
1.0654	6°.691	6.28
1.2176	8°.006	6.58
1.5220	11°.883	7.15
2.000	17°.00	8.50
2.500	25°.00	10.00

Table XLVII.—Conductivity Measurements.

$\mu\infty$ 0° = 117.2.

v.	μ_v 0°.	α.
13.13	90.90	77.5
6.57	85.14	72.6
3.25	76.00	64.8
1.64	68.60	58.5
1.31	61.90	52.8
0.90	55.30	47.2
0.82	52.28	44.6
0.65	45.29	38.6
0.50	34.25	29.2
0.40	26.11	22.3

Table XLVIII.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0761	25.2314	0.3477	24.8837	0.46
0.1522	25.5990	0.6955	24.9035	0.39
0.3044	26.1132	1.3910	24.7222	1.11
0.6088	27.2990	2.7819	24.5171	1.93
0.761	27.7974	3.4774	24.3200	2.72
1.0657	28.9284	4.8697	24.0587	3.76
1.2176	29.4458	5.5638	23.8820	4.47
1.522	30.6071	6.9548	23.6523	4.99
2.000	32.3305	9.1390	23.1915	7.23
2.500	34.0932	11.4237	22.6695	9.32
3.000	35.7096	13.7085	22.0011	12.00
3.394	36.9512	15.5093	21.4419	14.23

Table XLIX.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.0761	0.775	4.74	4.95	4.93	2.14	28.1
0.1522	0.726	4.56	4.93	4.91	3.96	26.0
0.3044	0.648	4.27	5.01	4.96	7.73	25.4
0.6088	0.585	4.04	5.37	5.27	12.97	21.3
0.7610	0.528	3.82	5.66	5.51	16.03	21.1
1.0654	0.472	3.61	6.28	6.04	22.35	22.0
1.2176	0.446	3.52	6.58	6.29	24.46	20.1
1.5220	0.386	3.30	7.15	6.79	28.55	18.8
2.000	0.292	2.95	8.50	7.89	34.71	17.4
2.500	0.223	2.69	10.00	9.07	39.08	15.6

Copper Chloride.

In the paper[1] to which reference has already been made, Jones and Getman attempted to calculate the approximate composition of the hydrates formed by copper chloride. In this calculation they had to make use of a part of the data obtained from other sources.

We have supplied this data for the various solutions, especially the specific gravities. We encountered difficulty in determining $\mu\infty$ for the copper salt. The value given was obtained by the conductivity method, taking into account the hydrolysis of copper chloride in dilute solutions.

The hydrating power of copper chloride is larger than would be expected from its water of crystallization. The increase in the amount of combined water, with the concentration, is seen in Table XLVIII. and in the curve in Fig. VIII., p. 563.

Table L.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.065	0°.331	5.09
0.1301	0°.639	4.91
0.2602	1°.273	4.89
0.5204	2°.711	5.29
0.7806	4°.413	5.65
1.3010	8°.395	6.45
1.5612	10°.383	6.65
1.8210	12°.960	7.12
2.0816	15°.480	7.43
2.6020	20°.820	8.00
3.000	25°.50	8.50
3.500	31°.50	9.00
4.371	44°.50	10.19

[1] THIS JOURNAL, 31, 353 (1904).

Table LI.—Conductivity Measurements.

$\mu\infty$ 0° = 120.

v.	μ_v 0°.	*α.*
15.30	94.42	78.7
7.64	88.06	73.4
3.84	78.38	65.3
1.92	67.68	56.4
1.28	59.30	49.4
0.76	48.22	40.2
0.64	39.32	32.8
0.55	35.02	29.2
0.48	30.81	25.7
0.38	22.58	18.8
0.33	17.48	14.6
0.29	13.05	10.9
0.23	7.61	6.11

Table LII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0651	25.1985	0.2189	24.9796	0.08
0.1301	25.3934	0.4378	24.9556	0.18
0.2602	25.7941	0.8756	24.9185	0.33
0.5204	26.5913	1.7512	24.8401	0.64
0.7806	27.3458	2.6268	24.7190	1.12
1.3010	28.8280	4.3780	24.4500	2.20
1.5612	29.5841	5.2536	24.3305	2.68
1.8210	30.2350	6.1231	24.1119	3.55
2.0816	30.9999	7.0048	23.9951	4.02
2.6020	32.4090	8.7492	23.6598	5.36
3.000	33.3949	10.0875	23.3074	6.77
3.500	34.7877	11.8187	22.9690	8.01
4.371	36.9809	14.6975	22.2834	10.87

Table LIII.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.1301	0.734	4.59	4.91	4.90	3.53	27.1
0.2601	0.653	4.29	4.89	4.87	6.62	25.4
0.5204	0.564	3.96	5.29	5.26	13.73	26.4
0.7806	0.494	3.69	5.65	5.59	18.88	24.2
1.3010	0.402	3.36	6.45	6.31	25.97	20.0
1.5612	0.328	3.08	6.65	6.47	28.94	18.6
1.8210	0.292	2.95	7.12	6.87	30.03	16.5
2.0816	0.257	2.82	7.43	7.13	33.58	16.1
2.6020	0.188	2.66	8.00	7.57	36.03	13.9
3.000	0.146	2.40	8.50	7.92	38.72	12.9
3.500	0.109	2.27	9.00	8.28	40.33	11.5
4.371	0.064	2.10	10.17	9.77	49.77	11.4

Copper Nitrate.

What was said about the earlier work on copper chloride holds also, to some extent, for copper nitrate. Jones and Getman[1] calculated the approximate composition of the hydrates for a few solutions of copper nitrate. The data used were, however, partly taken from the work of others and interpolation was often necessary.

We have now obtained, with the same solutions, all the data necessary for calculating the composition of the hydrates. We encountered the same difficulty in determining $\mu\infty$ for copper nitrate as for copper chloride and solved the problem, approximately, in the same way. The hydrating power of copper nitrate is just about what we should expect it to be from its water of crystallization (see Table I,II. and curve Fig. XI.).

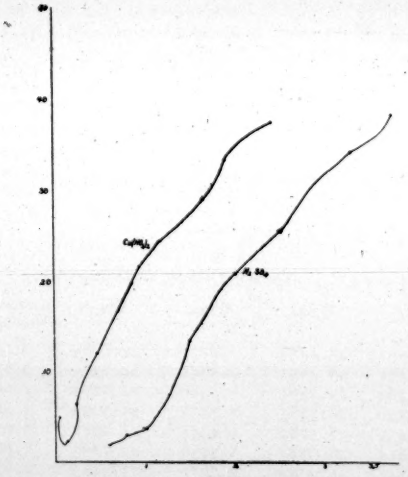


Fig. XI.

[1] THIS JOURNAL, 38, 353 (1904).

Table LIV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0591	0°.326	5.52
0.1182	0°.595	5.03
0.2363	1°.210	5.12
0.4726	2°.544	5.39
0.9452	5°.903	6.26
1.1815	7°.799	6.60
1.6541	12°.650	7.07
1.8904	15°.490	8.20
2.3630	21°.890	9.26

Table LV.—Conductivity Measurements.

$\mu\infty$ 0° = 118.

v.	μ_v 0°.	α.
16.90	99.36	84.2
8.46	93.05	78.9
4.23	82.97	70.3
2.12	73.16	62.0
1.05	58.45	49.5
0.84	52.34	44.4
0.60	40.70	34.5
0.52	35.84	30.4
0.42	26.70	22.6

Table LVI.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0591	25.1456	0.2772	24.8684	0.53
0.1182	25.3851	0.5543	24.8308	0.68
0.2363	25.8364	1.1086	24.7278	1.09
0.4726	26.7265	2.2172	24.5093	1.56
0.9452	28.5284	4.4344	24.0940	3.62
1.1815	29.3289	5.5436	23.7853	4.86
1.6541	31.0048	7.7613	23.2435	7.03
1.8904	31.9184	8.8698	23.0486	7.80
2.363	33.6390	11.0872	22.5518	9.79

Table LVII.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.1182	0.789	4.80	5.03	5.00	2.22	18.8
0.2363	0.703	4.48	5.12	5.07	6.47	27.4
0.4726	0.620	4.17	5.39	5.31	11.92	25.0
0.9452	0.495	3.70	6.26	6.03	21.47	22.7
1.1815	0.444	3.51	6.60	6.28	24.50	20.7
1.6541	0.345	3.14	7.07	6.55	28.92	17.5
1.8904	0.304	2.99	8.20	7.56	33.58	17.7
2.3630	0.226	2.70	9.26	8.35	37.59	15.9

Sulphuric Acid.

The approximate composition of the hydrates formed by sulphuric acid between the concentrations, normal and 4.37 normal, was calculated by Jones and Getman.[1]

We desired to learn what order of hydration existed in both very concentrated and very dilute solutions of sulphuric acid. The freezing-points of its solutions were measured up to a concentration of 5N by means of an alcohol thermometer, using solid carbon dioxide and alcohol or ether as the refrigerating agents. The results are given in Table LVI. and in the curve (Fig. XI., p. 577).

In dilute solutions no water is held in combination. From about 0.5 to 5N the amount of combined water increases with the concentration.

Table LVIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.10	0°.397	3.968
0.20	0°.670	3.850
0.30	1°.156	3.853
0.40	1°.570	3.920
0.60	2°.440	4.066
0.80	3°.300	4.125
1.00	4°.189	4.189
1.50	7°.443	4.962
2.00	11°.296	5.648
2.50	16°.275	6.510
2.73	21°.000	7.69
3.28	29°.000	8.84
3.825	41°.000	10.72
4.37	53°.000	12.13
4.50	58°.000	12.89
5.00	76°.000	15.20

[1] Z. physik. Chem., 49, 446 (1904).

Table LIX.—Conductivity Measurements.

$\mu\infty$ 0° = 500.

v.	μ_v 0°.	α.
10.0	305.0	61.0
5.0	282.0	56.4
3.33	280.0	56.0
2.50	273.6	54.7
1.67	264.8	52.9
1.25	257.0	51.4
1.00	253.4	50.7
0.67	221.25	44.25
0.50	199.42	39.9
0.40	178.79	35.8
0.37	175.54	35.1
0.30	147.50	29.5
0.26	127.70	25.5
0.23	105.50	21.1
0.22	100.21	20.0
0.20	86.97	17.4

Table LX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	25.1307	0.2452	24.8855	0.46
0.2	25.2355	0.4904	24.7451	1.02
0.3	25.4205	0.7356	24.6849	1.26
0.4	25.5761	0.9808	24.5953	1.62
0.6	25.8572	1.4712	24.3860	2.46
0.8	26.1187	1.9616	24.1571	3.37
1.00	26.5028	2.4520	24.0508	3.80
1.50	27.2753	3.6780	23.5973	5.61
2.00	27.9968	4.9040	23.0928	7.63
2.50	28.7102	6.1300	22.5802	9.68
2.73	28.9777	6.6885	22.2892	10.84
3.28	29.8027	8.0360	21.7667	12.53
3.825	30.4816	9.3836	21.0980	15.61
4.37	31.1640	10.7065	20.4575	18.17
4.50	31.5062	11.0340	20.4722	18.11
5.0	31.9335	12.2600	19.6735	21.26

Table LXI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	M.	H.
0.10	0.610	4.13	3.968	3.95	.....	.....
0.20	0.564	3.96	3.850	3.81	.....	.....
0.30	0.560	3.94	3.853	3.80	.....	.....
0.40	0.547	3.89	3.920	3.86	.....	.....
0.60	0.529	3.83	4.066	3.97	1.96	3.3
0.80	0.514	3.77	4.125	3.99	3.12	3.9
1.00	0.507	3.75	4.189	4.03	3.86	3.9
1.50	0.443	3.52	4.962	4.68	13.17	9.2
2.00	0.399	3.27	5.648	5.22	20.75	10.4
2.50	0.358	3.19	6.510	5.81	25.42	10.2
2.73	0.351	3.17	7.690	6.86	29.88	10.6
3.28	0.295	2.96	8.840	7.73	34.28	10.4
3.825	0.255	2.81	10.720	9.05	38.31	10.0
4.37	0.211	2.64	12.130	9.93	40.79	9.4
4.50	0.200	2.60	12.890	10.56	41.88	9.3
5.00	0.174	2.51	15.200	11.97	43.95	8.6

General Discussion of the Results.

It must be remembered that the problem of calculating even the approximate composition of the hydrates existing in solution is difficult. Some of these difficulties have already been mentioned. Certain assumptions must be made which are only approximately true. This is the case especially with the law of Raoult, which probably does not hold rigidly for concentrated solutions. Further, it has already been pointed out that the conductivity method is only a rough measure of the dissociation in concentrated solutions.

Taking all of the difficulties into account, we are still of the opinion that we can get a fairly good idea as to the composition of the hydrates, formed by the various electrolytes, in aqueous solutions of different concentrations.

An examination of the results recorded in this paper will show that the amount of water, held in combination by the dissolved substance, increases as the concentration of the solution increases. This is, of course, what would be expected in terms of mass action.

The number of molecules of water in combination with 1

molecule of the dissolved substance sometimes increases from the most concentrated to the most dilute solution, as with magnesium chloride and bromide, manganese chloride, nickel chloride and copper chloride.

With some substances the number of molecules of water held in combination by 1 molecule of the dissolved substance may pass through a well-defined maximum as the dilution is increased. In other cases, the number of molecules of water held in combination by 1 molecule of the dissolved substance may reach a maximum value as the dilution is increased; this maximum value may then remain practically constant with further increase in the dilution. Examples of all of these conditions are to be found in the substances discussed in this paper. The probable explanation of these facts will appear in a subsequent communication.

An examination of the curves, Figs. V. to XI., will show that they are all of the same general type. These express the relation between the total amount of water in combination and the concentration of the solution. This resemblance in type is what we would expect, because the total amount of water held in combination by the dissolved substance is undoubtedly subject to the law of mass action.

Nature of the Compounds Formed.

The question arises whether these hydrates are true chemical compounds, as that term is ordinarily used, or whether they represent some less stable form of combination? That they are unstable is shown by the ease with which they are broken down by heat. Most of the water can be driven off, from the above solutions, at a temperature only a little above 100°. The more complex hydrates are, then, decomposed in solution at a comparatively low temperature and the water given off in the form of vapor. In the light of these facts the hydrates can scarcely be regarded as true chemical compounds. If, however, we insist on calling them chemical compounds, we must admit that they represent a very low order of stability.

A New Line of Evidence for the Theory.

The hydrates in solution are, as we have just seen, very unstable at the higher temperatures. *These hydrates become more and more stable the lower the temperature.* Hence, we might expect dissolved substances to be capable of bringing more and more water with them out of solution, the lower the temperature at which the crystals were formed.

An examination of the literature shows that this is the case. There is a comparatively large number of cases on record of salts crystallizing with different amounts of water; the lower the temperature at which the crystals were formed, the larger the number of molecules of water of crystallization.

This is exactly what we should expect from our theory of hydrates in aqueous solutions and from the increased stability of these hydrates as the temperature is lowered.

While the number of cases on record bearing on this point is large, we hope to be able to increase it in the near future. We shall make a systematic study of the problem in this laboratory, to see how greatly water of crystallization may be varied by crystallizing the salt at as widely different temperatures as possible.

Do Ions or Molecules Form Hydrates?

We are still of the same opinion as was expressed in the last communication[1] on this subject, that both the molecules and ions combine with water forming hydrates. It seems that the molecules are certainly capable of forming hydrates, because, in very concentrated solutions, where the molecules are present in large quantities, we often have considerable hydration and, further, Jones and Getman[2] have shown that certain non-electrolytes, such as glycerol, acetamide, fructose, etc., which are undissociated, still have the power of combining with water in solution, forming hydrates of even a high order of complexity.

That ions are capable of combining with water in solution, is shown by the magnitude of the hydration in many of the dilute solutions, where chiefly ions and only a few molecules are present.

[1] Jones and Getman: Z. physik. Chem., 49, 451 (1904).

[2] THIS JOURNAL, 32, 308 (1904).

Attention should be called to the fact that, in the preceding tables, the number of molecules of water in combination with 1 molecule of the dissolved substance is calculated for a molecule of the dissolved substance. If this molecule is dissociated into 2, 3, or 4 ions, the number given in column H in the tables would have to be divided by 2, 3, or 4, in order to ascertain how many molecules of water were in combination with an ion resulting from the dissociation of the molecule in question.

The Old and the New Hydrate Theory.

The theory of hydrates in aqueous solution that we believe to have established by the work, of which this is only a chapter, is to be sharply distinguished from the old hydrate theory of Mendeléeff, which, having long since been shown to be untenable, has been abandoned. According to the older theory, when a substance, like calcium chloride, is dissolved in water, there are formed certain definite chemical compounds, with perfectly definite amounts of water.

According to the theory established by this work, the compounds formed are, at best, very unstable and vary in combination all the way from 1 molecule of water to a very great number. The composition of the hydrate formed by any given substance is purely a function of the concentration of the solution, or is determined, as we say, by the effect of mass action. Thus, the composition of the hydrates formed by calcium chloride may vary all the way from a few molecules of water up to at least 30 molecules and may have all intermediate compositions, depending solely upon the concentration, temperature being, of course, understood to be constant.

It is thus obvious that the older and the newer hydrate theories are fundamentally different in character.

Summary.

1. Some of the evidence for the existence of hydrates in aqueous solutions of electrolytes has already been pointed out in earlier papers. The most direct and convincing evidence is to be found in the relation between the water of crystallization

and the magnitude of the freezing-point lowering. The plates of curves that bring out this relation, together with a brief discussion of the results, are given at the beginning of the present paper.

2. The chief object of this part of the investigation is to calculate, as closely as possible, the amount of water that is in combination with the dissolved substance at the various concentrations of the solutions. In the earlier preliminary calculations certain assumptions had to be made, for lack of sufficient data. This data we have now supplied, as far as possible, for 15 of the electrolytes with which we had already worked.

3. The amount of water held in combination by the dissolved substance increases with the concentration of the solution. That this increase is regular, to within the limits of experimental error, is shown by the curves, Figs. V. to XI.

4. The amount of water combined with 1 molecule of the dissolved substance, in some cases increases from the most concentrated to the most dilute solution. In other cases it passes through a maximum, in still others it acquires a maximum value, which remains practically constant with further increase in the dilution of the solution.

General Significance of the Results.

These results certainly have a direct bearing on the whole subject of solutions. They afford, at least, a partial explanation of the apparent failure of the gas laws to hold for concentrated solutions. Such solutions are obviously much more concentrated than we should suppose them to be from the amount of dissolved substance that is present in them. A part of the water present being in combination, there is just so much less water left in the solution to play the rôle of solvent and the solution is concentrated by just this amount. In the case of nearly every substance which crystallizes with a large amount of water, this change in concentration is large and, in many cases, of enormous magnitude.

Future Work.

We shall take up a much larger number of substances; at first those for which data have been partially determined in earlier investigations in this laboratory and calculate, as closely as possible, the composition of the hydrates formed. We shall then bring within the scope of this investigation many new substances upon which we have not yet had time to work.

We propose also to study the effect of one substance, with large hydrating power, upon another with smaller power to form hydrates, when both are simultaneously present in the solution. Indeed, the number of problems that are opened up as the result of showing that combination between solvent and dissolved substance takes place, is almost unlimited.

We propose to extend this work much farther, to solvents other than water.

This investigation was carried out under a grant from the Carnegie Institution, to which we take this opportunity of extending our thanks.

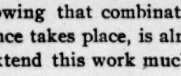
CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
December, 1904.

THE HYDRAZINE DERIVATIVES OF TETRACHLORPHTHALIC ACID.

BY ISAAC KING PHELPS.

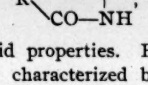
At the suggestion of Professor Theodor Curtius, the following investigation of hydrazine derivatives of tetrachlorphthalic acid was undertaken. A considerable part of the work was done in the laboratory of the University of Heidelberg, in the summer semester of 1902.

These hydrazine derivatives of tetrachlorphthalic acid appear to follow the typical reactions of hydrazine derivatives of organic dibasic acids,[1] in general methods of formation, giving substances of the primary type,



and also the usual secondary hydrazides of the type

[1] Curtius, Schöfer and Schwan: J. prakt. Chem., **31**, 187 (1895). Curtius and Foersterling: *Ibid.*, **31**, 371 (1895).



with characteristic acid properties. Both classes of derivatives of this acid are characterized by high melting-point, stability and inertness.

The neutral ester of tetrachlorphthalic acid, prepared by acting upon the silver salt of the acid with ethyl iodide and crystallizing from alcohol, reacts very slowly with hydrazine hydrate. The product proved to be the primary hydrazide of the acid, combined with 1 molecule of hydrazine. In general, the primary hydrazides[1] of organic dibasic acids are basic in properties, forming compounds with 2 molecules of a monobasic acid, but the primary hydrazide of tetrachlorphthalic acid shows acidic power in combining, as it does, with the strongly basic hydrazine. Further, the substance so formed is quite stable toward heat, showing an effect first at 290°; by treatment with aqueous hydrochloric acid it loses the molecule of hydrazine of combination, but does not take up halogen acid, even when treated with acid of 1.20 sp. gr.

The acid ester of tetrachlorphthalic acid was prepared by boiling tetrachlorphthalic acid with absolute alcohol. When this product was treated with hydrazine hydrate the reaction was slow, resulting finally in the formation of a number of substances. Although tried under varying conditions, no definite new derivatives were isolated.

By treating tetrachlorphthalic acid with hydrazine hydrate and heating, the secondary hydrazide results. It is also a stable substance, acts as a weak monoacidic base and dissolves in aqueous potassium or sodium hydroxide solutions, but not in sodium carbonate or ammonium hydroxide solutions.

EXPERIMENTAL.

Primary Hydrazide Combined with Hydrazine, $C_6Cl_4(CONHNH_2)_2.N_2H_4$.—Diethyl tetrachlorphthalate (0.75 gram) was heated with 0.26 gram of hydrazine hydrate (b. p. 119°) (1 mol. : 1 mol.) with 1 cc. of ether, in a sealed tube, at

[1] *Loc. cit.*

100°, for 10 hours. The yellow crystals which had separated were filtered off and washed with ether, in which they were insoluble; from the filtrate and ether washings 0.5 gram of solid material was obtained which was crystallized once from alcohol and was recognized by the melting-point, 59°, as composed chiefly of unchanged ester. The yellow, crystalline material, insoluble in ether, was found to be slowly and difficultly soluble in hot alcohol, from which it crystallized, on cooling, in fine, feathery needles. It charred slowly at 290°–300°, without melting. Analysis:

0.0812 gram substance gave 17 cc. moist N at 20° and 755.6 mm.

	Calculated for $C_8H_{10}O_2Cl_4N_6$.	Found.
N	23.12	23.81

Primary Hydrazide, $C_6Cl_4(CONHNH_2)_2$.—The hydrazine salt of the primary hydrazide above described was treated with a hot alcoholic solution of hydrochloric acid, in excess and boiled; the yellow substance lost its color but remained insoluble. It was filtered off, washed and dried *in vacuo*. It was insoluble in the common organic solvents and also in concentrated hydrochloric acid. Analysis:

0.1849 gram substance gave 29 cc. moist N at 23° and 758 mm.

	Calculated for $C_8H_6Cl_4O_2N_4$.	Found.
N	16.90	17.63

Secondary Hydrazide, $C_6Cl_4(CONH)_2$.—Tetrachlorphthalic acid (5 grams) and hydrazine hydrate (1.23 grams) (1 mol : 1.5 mol.) were heated together under a return condenser, in an oil-bath, at 140°–150° for half an hour. The cooled, slightly yellow residue was thoroughly extracted with hot water. The product was insoluble in the common organic solvents—excepting only glacial acetic acid, from which it was obtained in pale-yellow crystals, on cooling the hot solution. It melted, with slight decomposition, at 286°–287° and dissolved in aqueous sodium and potassium hydroxide solutions, from which it was precipitated, unchanged, by acids. Analysis:

0.1774 gram substance gave 14.8 cc. moist N at 21° and 754 mm.

	Calculated for $C_8H_3O_2N_2Cl_4$.	Found.
N	9.36	9.42

0.1673 gram substance gave 0.3161 gram AgCl (Carius).

	Calculated.	Found.
Cl	46.85	47.28

The Diacetyl Derivative, $C_6Cl_4(CONCOCH_3)_2$.—The secondary hydrazide (2 grams) and acetic anhydride (4 grams) (1 mol. : 6 mol.) were boiled for 3 hours, under a return condenser. The solid material, formed on cooling, was crystallized twice from alcohol. It melted at 203°–204°. Analysis:

0.1690 gram substance gave 11 cc. moist N at 17° and 755 mm.

	Calculated for $C_{12}H_6O_4N_2Cl_4$.	Found.
N	7.32	7.50

The Sodium Salt of the Secondary Hydrazide, $C_6Cl_4(CON)_2HNa$.—The crude, secondary hydrazide (3 grams) was dissolved in a slight excess of sodium hydroxide solution, precipitated with aqueous hydrochloric acid and washed carefully on a filter. The freshly prepared material was treated with sodium hydroxide solution, made by treating the metal with alcohol and diluting with water, in amount insufficient to dissolve it. The excess of the hydrazide was filtered off, the filtrate evaporated and, finally, the solid dried in a vacuum, over sulphuric acid. Analysis:

0.2520 gram salt gave 0.0546 gram Na_2SO_4.

	Calculated for $C_8HCl_4O_2N_2Na$.	Found.
Na	7.16	7.02

The Potassium Salt of the Secondary Hydrazide, $C_6Cl_4(CON)_2HK$.—The potassium salt was similarly prepared—with the single exception that commercially pure hydroxide was used, instead of that obtained from the metal. This product differed from the sodium salt in being slightly more readily soluble in water. Analysis:

0.2153 gram salt gave 0.0551 gram K_2SO_4.

	Calculated for $C_8HCl_4O_2N_2K$.	Found.
K	11.58	11.49

The Silver Salt of the Secondary Hydrazide, $C_6Cl_4(CON)_2HAg$.—The sodium salt was dissolved in water and treated with a slight excess of a solution of silver nitrate. The white precipitate was filtered off, washed carefully with water and dried in darkness, over sulphuric acid, in a vacuum. Analysis:

0.1198 gram salt gave 0.0413 gram AgCl.

	Calculated for $C_8HCl_4O_2N_2Ag$.	Found.
Ag	26.50	26.95

Ethyl Carboxylate of the Secondary Hydrazide, $C_6Cl_4(CON)_2HCOOC_2H_5$.—A mixture of 2 grams of the silver salt with 10 cc. of ethyl chlorcarbonate was boiled under a return condenser, for 8 hours; the excess of ester wa allowed to evaporate spontaneously and the solid residue extracted with hot alcohol. The white, prismatic crystals, which appeared on cooling the solution, melted at 244°–245°. Analysis:

0.1420 gram substance gave 9.9 cc. moist N at 20° and 760.5 mm.

	Calculated for $C_{11}H_6O_4Cl_4N_2$.	Found.
N	7.55	7.98

Although, in the benzene nucleus of the compounds above described, chlorine is fully substituted and although hydrazine hydrate is a strong base, in no case was an indication observed of a reaction between the hydrazine and the halogen in the ring.

The author gratefully acknowledges his indebtedness to Professor Theodor Curtius for many helpful suggestions.

KENT CHEMICAL LABORATORY,
NEW HAVEN, CONN.

AN ELECTRICAL METHOD FOR THE COMBUSTION OF ORGANIC COMPOUNDS.

By H. N. Morse and L. S. Taylor.

The process for the analysis of organic compounds, which is here described, has been in general use in this laboratory during the past year and with such satisfactory results that it has almost wholly supplanted the older method of burning organic compounds. It has already been applied to the combustion of hydrocarbons and their oxygen, halogen, nitrogen and sulphur derivatives. The advantages which it has been found to possess, over the usual method, are the following: (1) The apparatus required is so compact and of such small dimensions, that the combustions can be made at the working table of the student; (2) the waste of heat energy is much smaller; (3) the time consumed in preparing for and in making a combustion is considerably diminished.

Fig. I. (p. 594) represents the apparatus in its simplest form. The thin glass combustion tube is closed at one end and has a length of 350 mm. and an internal diameter of 15 mm. Through the rubber stopper in its open end there pass: (1) The porcelain tube *c*, which has a length of 250 mm. and a diameter of 6 mm.; (2) the glass tube *k*, through which the products of combustion enter the absorption apparatus; (3) the rather stout platinum wire (No. 18 B & S gauge), which extends from *f* to *j*. The porcelain tube *c* is joined outside of the stopper, by means of rubber tubing, to the branched glass tube *d*. The latter is provided with a stopper, *g*, through which passes the platinum wire *e* (also No. 18), which extends into the porcelain tube to the point *h*, where it is joined to a smaller platinum wire (about No. 29, B & S gauge). The smaller wire has a length of about 1.75 meters and weighs, approximately, 2.5 grams. It extends, from its junction with the larger wire at *h*, through the porcelain tube to the inner end of the latter and then returns on the outside, in a series of suspended coils, to the point *j*, where it joins the larger wire *f*. Thicker wire is used from *f* to *j* and from *e* to *h* in order to avoid any overheating of the rubber stopper by the current.

The roll of copper wire gauze *b*, about 60 mm. in length, is inserted between the end of the porcelain tube and the boat containing the substance to be burned.

The oxygen or air, which is used in the combustion, enters the apparatus at *d* and while passing over the portion of the small wire which is within the porcelain tube, has its temperature raised more or less, according to the rate of its flow. It is, therefore, already hot when it enters the tube *c*, where the combustion is to be effected. The excess of the oxygen and the products of the combustion pass together over the heated coils on the outside, completing the burning of any unoxidized material coming from the rear.

In the earlier work with this apparatus we employed stems of long clay tobacco pipes, but, owing to the highly porous character of this material, it was found necessary, in order to obtain satisfactory determinations of hydrogen, to dry out the tube each time before beginning a combustion. We afterwards substituted for the pipe stems unglazed porcelain tubes, which were made for us at the Royal Berlin Porcelain Works. These have proved very durable and they are not, of course, hygroscopic to an appreciable degree. None of these porcelain tubes has yet cracked, though some of those in use have served for more than a hundred combustions.

The roll of copper wire gauze, *b*, is not absolutely necessary when the substances to be burned do not readily yield explosive mixtures with oxygen and, in our earlier work, it was omitted. Its presence is, however, of advantage because much less care is required in the management of the combustion with it than without it. If the substances are liquids, or if they readily yield large quantities of inflammable vapors when heated, the roll of wire gauze must be inserted between the material and the end of the porcelain tube through which the oxygen enters. There is one objection and only one, to its use, this is that the flow of oxygen or air must be continued for some time after the completion of the combustion, in order to insure the removal of all of the carbon dioxide and water from the space occupied by the boat.

The combustion is conducted in the following manner: Having placed, in the positions indicated in the figure, the boat containing the material and the roll of copper wire gauze (which, in the beginning, may or may not be oxidized) and having joined the tube *k* to the usual train of absorption apparatuses, a slow current of dry and purified oxygen is admitted and the electric circuit is closed through a regulating rheostat. The flow of the current is gradually increased until the wire coils assume a bright red color, then the roll of gauze, *b*, is heated by means of a gas lamp giving a broad, thin flame, to a temperature at which the copper is readily oxidized by the hot oxygen issuing from the porcelain tube. The substance in the boat is then heated with the same lamp, or with another which is held in the hand. The rate of heating and the flow of oxygen are so regulated with respect to each other that at least one-half of the roll of wire gauze is kept in the oxidized condition during the entire combustion. After the formation of volatile products has ceased, the reoxidation of the copper progresses rapidly and the oxygen enters the rear compartment, burning any residue of carbon in the boat or upon the glass. Having finished the combustion of the substance, the current of oxygen is replaced by one of dried and purified air, the flow of which must, of course, be continued until the products of combustion have all been expelled from the space behind the roll of wire gauze. It is here that a miscalculation is likely to be made. The time required for the complete removal of these products depends, principally, upon the freedom of diffusion through the gauze and for this reason it should not be rolled too tightly.

The apparatus, as already described, is adapted to the combustion of those solids and liquids which consist of carbon and hydrogen, or of carbon, hydrogen and oxygen.

The heating of the roll of wire gauze *b*, and, at times, of the substance also, is facilitated by inverting over the tube, at a little distance above it, a trough of asbestos board, the side of the trough, at the back, being much deeper than that in front. This arrangement is supported in its position by a rod, which

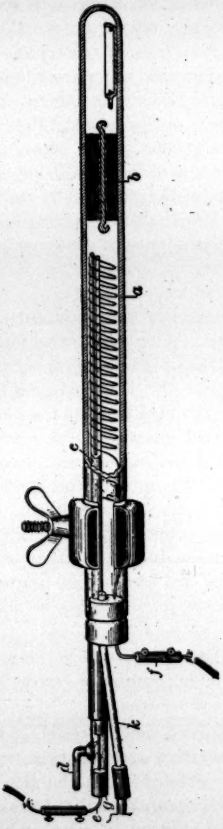


Fig. I.

Fig. II.

is inserted in a heavy block, resting upon the work table behind the tube. The device is also of advantage in protecting the tube from draughts of cold air during the combustion and during the subsequent cooling period. The portion of the glass tube which is occupied by the porcelain tube and the platinum wire is protected, on the bottom, by a semi-circular strip of asbestos board which is inserted in the clamp between the lower jaw and the glass. To protect the upper portion of the tube in the same region, a semi-circular trough of mica is inverted over it, behind the clamp, in such a manner that the lower edges of the mica rest in the asbestos trough below. The mica is made to keep its curved form by riveting it to narrow strips of metal and then bending the latter to the required shape.

The cooling of the tube requires some care. The current should be reduced quite gradually and it is well, also, as soon as the combustion is finished, to cover the portions of the glass tube which is beyond the porcelain one with the soot from a smoky flame and to take any other measures for the protection of the tube which will contribute toward the proper annealing of the glass. Care must likewise be taken never to allow the platinum loops to come in contact with the glass either while heating or cooling the tube, because, in the former case, the metal is likely to stick to the glass, while, in the latter, the tube is quite sure to crack at some lower temperature. If the loops are too large, the wire should be taken out and rewound.

The time required for a combustion does not, ordinarily, exceed half an hour and it may be reduced to 20 minutes, or even less, if the substance to be burned is of such a character that the roll of wire gauze can be dispensed with. We do not, however, recommend its omission at any time, except to those who have had some experience with the method.

The consumption of electrical energy is small, amounting to about 3.6 amperes at 54 volts (194.4 watts, or one-third of a horse power) during the time when the highest temperature is maintained.

At the highest temperatures employed during the combustion (at a bright red, but not a white heat), especially when

the wire is new, there is a sensible volatilization of the platinum. This volatilization of platinum in an atmosphere of oxygen, at comparatively moderate temperatures, has been repeatedly noticed by others. In one case, a platinum wire weighing, in the beginning, 2.3446 grams was found, at the end of the thirty-eighth combustion, to have lost 0.1337 gram in weight. The volatilized metal settles upon the surfaces of the glass and porcelain tubes as a dark deposit which, at first, may be mistaken for carbon. The presence of such films of volatilized platinum upon the inner surface of the tube is, of course, of some assistance in the combustion.

The obvious objections to the use of the short closed combustion tube represented in Fig. I. are the following: In the first place, whenever the boat is to be introduced or withdrawn, it is necessary to remove and reinsert the rubber stopper with the tubes and wires which pass through it and also the roll of wire gauze and, during such manipulation, the wire loops, which should be distributed uniformly along the porcelain tube, are easily displaced and may become entangled. Again, as previously mentioned, the flow of air must be continued for some time after the combustion is otherwise finished, in order to insure the complete removal of carbon dioxide and water from the space occupied by the boat. These difficulties are wholly obviated by using a somewhat longer tube which is open at both ends, as represented in Fig. II. In this arrangement the boat is introduced from the rear and there is placed behind it a second roll of copper wire gauze. The stopper in the front end of the combustion tube, the forward roll of wire gauze and also the apparatus as a whole, are never disturbed. Each roll of wire gauze is heated by a lamp giving a broad, thin flame and there is inverted over both rolls and the space between them the asbestos shield already described. The lamps should be raised until the bottom of the tube is just within the blue region of the flames. To prevent any sagging of the combustion tube while hot, it is supported at a point beneath the end of the porcelain tube by a forked or notched standard, which is placed under the asbestos trough in which the front portion of the apparatus lies.

The combustion is conducted in much the same manner as in the short closed tube, except that a slow current of air or oxygen is admitted from the rear during the entire experiment. This prevents any accumulation of volatilized matter in the back part of the tube and aids in the expulsion of the products of combustion from the space occupied by the boat.

If the substance to be burned is very volatile, it is advisable to introduce air and not oxygen at the rear and to employ, behind the boat, a roll of gauze which is only partially oxidized. In this way the vapors of the substance may be diluted with nitrogen to any desired extent.

The clamp at the rear is required only as a support and it should not be made to grip the tube so tightly as to prevent the free movement of the latter, back and forth through the former.

In the following determinations of carbon and hydrogen in cane-sugar, which were made for the purpose of testing the method, the short closed tube was employed and the roll of wire gauze was omitted. A clay tobacco pipe stem served for the introduction of oxygen and the effect of its use is evident in the high percentages of hydrogen which were obtained in the first four analyses. In the last two analyses, in which normal quantities of hydrogen were obtained, the pipe stem was thoroughly burned out in a current of oxygen before beginning the combustion:

Weight of sugar. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1364	41.95	6.86	25
0.1188	42.03	6.63	18
0.1227	42.03	6.65	18
0.1382	42.07	6.73	18
0.1154	42.11	6.47	18
0.2809	42.03	6.46	45
Theoretical,	42.09	6.47	

The current at the highest temperature was 2.6 amperes at 48 volts.

Careful management is required, even in the combustion of such substances as sugar, when the roll of wire gauze is

omitted. On several occasions, when it was attempted to reduce the time consumed in the combustion to 15 minutes or less, small explosions occurred and the dilute solution of palladium chloride in the Geissler apparatus, which was always attached to the end of the absorption train, darkened in color. Hence the combustion tube was lengthened slightly and the roll of wire gauze previously mentioned was inserted between the boat and the end of the porcelain tube. Combustions of toluene and two of naphthalene were made with the modified apparatus with the following results :

Toluene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1057	90.91	8.62	35
0.065	91.25	8.80	35
Theoretical,	91.24	8.76	

Naphthalene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen Found. Per cent.	Time occupied in combustion. Minutes.
0.1184	93.54	6.36	55
0.1252	93.49	6.39	55
Theoretical,	93.70	6.36	

During the first attempt to burn naphthalene a slight deposit of the substance collected in the front end of the tube. The length of the small platinum wire was, therefore, increased by about 0.5 meter, making its total length about 2 meters. No further difficulty was experienced in effecting complete combustions. With the lengthened wire, the electrical energy consumed, at the highest temperature, was 3.6 amperes at 65 volts. The wire was afterwards shortened until, with a current of 3.6 amperes, the fall in potential was 54 volts.

The analyses of naphthalene and benzene, which follow, were made with the apparatus represented in Fig. II.

Naphthalene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1274	93.59	6.83	45
0.1340	93.50	6.80	30
0.1198	93.51	6.46	30
0.1249	93.57	6.36	35
Theoretical,	93.70	6.36	

Benzene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.0887	92.24	7.82	40
0.1474	92.28	7.80	75
0.1749	92.20	7.87	75
0.1334	92.18	7.66	75
Theoretical,	92.25	7.75	

The Combustion of Substances Containing Nitrogen.

For the determination of carbon and hydrogen in compounds containing nitrogen, there are placed in the combustion tube: (1) a roll, 100 mm. in length, of copper wire gauze which has been reduced in the usual way by methyl alcohol; (2) a roll, 80 mm. in length, of wire gauze which has been well oxidized; (3) the boat containing the substance; (4) a short roll of wire gauze also well oxidized.

During the combustion each of the three rolls is heated by a burner giving a broad, thin flame, the last lamp serving also for heating the substance. The portion of the tube occupied by the copper is covered by a screen of asbestos board, to insure a sufficiently high temperature for the reduction of nitric oxide. The flow of oxygen through the porcelain tube is so regulated that only about one-quarter of the copper roll *b*, is oxidized, while at the rear it is admitted as rapidly as may be necessary to keep a portion of the second roll at all times in an oxidized condition.

No great difficulty has been experienced in successfully burning nitrogenous compounds, except in the case of nitro derivatives and even these gave good results after we adopted the practice of introducing into the boat, with the

substance, a quantity of loose copper oxide or finely divided silica.

By way of testing the applicability of the method to compounds containing nitrogen, analyses were made of urea, uric acid, orthonitrophenol and metadinitrobenzene. The results are given below:

Urea.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1237	19.87	6.79	60
0.1542	20.03	6.78	70
0.1569	19.90	6.78	60
Theoretical,	19.96	6.70	

Uric Acid.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1947	35.64	2 68	75
0.1738	35.60	2.68	75
0.1970	35.65	2.62	
0.1929	35.60	2.42	
Theoretical,	35.67	2.39	

Nitrophenol.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.2632	51.69	3.75	75
0.1520	51.62	3.89	75
0.1225	51.78	3.76	60
0.1315	51.78	3.76	70
0.1464	51.75	3.79	60
Theoretical,	51.77	3.62	

Dinitrobenzene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1152	42.75	2.61	90
0.1435	42.70	3.02	120
0.1441	42.67	2.62	105
0.1174	42.72	2.78	120
0.1462	42.73	2.72	120
Theoretical,	42.83	2.39	

The time consumed in the burning of these nitrogenous compounds, especially of the dinitrobenzene, was probably greater than necessary; but some of our earlier experiences had convinced us that, in order to secure a complete reduction of the nitric oxide, the carbon must be entirely burned before the products of the combustion reach the reduced roll *b*, of wire gauze.

The Combustion of Halogen Compounds.

To prepare the apparatus for the analysis of substances containing the halogens, a piece of silver foil, about 50 mm. in width, is rolled up with a sheet of thick paper, which is afterwards withdrawn. The silver roll is placed in the tube quite close to the end of the porcelain tube and is not directly heated during the combustion. In other respects the arrangements are the same as for the combustion of non-nitrogenous compounds. A roll of well oxidized copper wire gauze follows the one of silver, then the boat containing the substance and, finally, a second roll of oxidized copper wire gauze.

During the combustion there is formed a quantity of fusible cuprous-halogen salt, which deposits itself more or less upon the inner surface of the glass tube, but does not, at any time, get beyond the roll of silver foil into the space occupied by the porcelain tube and platinum wire. On cooling, the cuprous-halogen salt, in accordance with the well-known behavior of such compounds, absorbs large quantities of oxygen, only to give it up again when the apparatus is reheated in a succeeding experiment. At the same time the copper wire, in the oxidized rolls, grows thinner and becomes quite brittle.

The quantity of the cuprous salt accumulates, after a few combustions, to such an extent that the time required for its oxidation is considerable. Hence, it is well to cleanse the combustion tube frequently and to renew, at the same time, the oxidized rolls of copper wire gauze.

The substances selected for the purpose of testing the applicability of the method to halogen compounds were dibrombenzene and chloral ethylate. The results are given below:

Dibrombenzene.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.
0.1245	30.62	1.85
0.1395	30.40	1.82
0.1319	30.33	1.75
0.0836	30.40	1.93
0.0745	30.42	1.81
Theoretical,	30.51	1.71

Time of combustion about 30 minutes.

Chloral Ethylate,
$CCl_3CH(OH)OC_2H_5$.

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.
0.1611	24.83	3.63
0.1765	24.90	3.64
0.1789	24.61	3.71
0.1570	24.73	3.83
Theoretical,	24.82	3.64

Time of combustion about 30 minutes.

The Combustion of Sulphur Compounds.

The determination of carbon and hydrogen in compounds containing sulphur presents no difficulty. A large number of such analyses have been made in this laboratory within the past year and the results have been quite as satisfactory as those obtained by the older method. The only change which it is necessary to make in the simple arrangement for non-nitrogenous and non-halogen compounds, in order to adapt the method to the combustion of sulphur compounds, is to substitute lead chromate for the roll of oxidized copper wire gauze which is nearest to the end of the porcelain tube. Instead of maintaining the lead chromate in its position in the tube by means of plugs of asbestos or of wire gauze, it has been found more convenient and better for the glass tube to introduce it in the form of a cartridge. This is prepared by filling, with the loose, granular chromate, a shell made from fine copper wire gauze.

The first analyses of sulphur compounds were made with

diphenylsulphone as the material. The results are given below :

Weight of substance. Gram.	Carbon found. Per cent.	Hydrogen found. Per cent.	Time occupied in combustion. Minutes.
0.1035	65.93	4.63	30
0.0997	66.00	4.70	45
0.1021	65.89	4.73	60
0.0961	65.98	4.53	45
Theoretical,	66.01	4.61	

JOHNS HOPKINS UNIVERSITY,
March 1, 1905.

Contribution from the Chemical Laboratory of the University of Illinois.

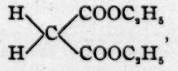
A CONVENIENT AND PRACTICAL METHOD FOR MAKING THE ESTER OF MESOXALIC ACID.

BY RICHARD SYDNEY CURTISS.

At present there exists no good and easy method for the preparation, in quantity, of diethyl mesoxalate. The two ways of making it, as given by Beilstein, are : (*a*) The distillation of acetylbromtartronic ester ;[1] (*b*) the action of ethyl iodide on silver mesoxalate.[2] Both are costly methods.

Bouveault and Wahl[3] have, more recently, discovered that it can be obtained by the action of nitric oxide on diethyl isonitrosomalonate. The yield is not given.

This difficulty in its preparation has resulted in a search for some other method which would give a good yield, at a less cost in time and material. Manifestly the simplest way, theoretically possible, to make diethyl mesoxalate is to convert the two methylene hydrogen atoms of malonic ester,



into hydroxyl groups.

It has been found that this can be accomplished easily, by

[1] Conrad and Brückner : Ber. d. chem. Ges., 24, 3000.
[2] Petrieff : J. russ. chem. Ges., 10. 75.
[3] Compt. rend., 137, 196.

saturating the ester, at —15°, with the gaseous red oxides of nitrogen, obtained from arsenic trioxide and nitric acid and filtering off the crystals, which are deposited in fair quantity, after the mixture has stood a few hours.

This product, once recrystallized, is pure diethyl mesoxalate, as shown by its melting-point, 57°, its analysis, the formation of a potassium salt by saponification and of a yellow phenyl hydrazone from the latter, corresponding in melting-point to that of the phenyl hydrazone of mesoxalic acid.

The above treatment of diethylmalonate leads to the formation of a number of other products. A study of these, the use of other oxidizing agents and also of the various reactions of mesoxalic ester as a ketone is in progress.

URBANA, ILL.,
April 8, 1905.

ON THE PINACONE-PINACOLIN REARRANGEMENT.

BY P. J. MONTAGNE.

The preliminary publication by Acree[1] induces me to make the following remarks:

Acree discusses the question, whether the pinacone-pinacolin, or other similar rearrangements, can take place through ring formation, as first suggested by Coutourier and subsequently by others. This suggestion being applied to aromatic derivatives, the group in the nucleus would prove, in that case, to have changed its position after the reaction. Acree intends to determine the position of the group in the nucleus before and after the migration and to solve the question in that way.

In April, 1901, however, I treated this same question at the "Nederlandsch Natuur-en Geneeskundig Congres" at Rotterdam (Dutch Physical and Medical Congress) and solved it with respect to two examples. Two articles on this subject have been published.[2] I have ascertained that, in the case of benzil, as well as of hydrobenzoin, the group in the nucleus does not change its position after the migration, a ring formation, being, consequently, impossible. In view of an

[1] This JOURNAL, **33**, 180 (1905).
[2] Rec. Trav. Chim., **21**, 6, 30.

explanation given by Nef, I announced, in the article above mentioned, the solution of this problem for the benzpinacone. As the result of my investigation of the subject, I stated that, in the rearrangement of this substance, the group in the nucleus retained its place. This article has recently been published.[1]

I am trying now to solve the same problem in the case of other compounds.

DEVENTER, HOLLAND,
April, 1905.

REVIEWS.

A SELECT BIBLIOGRAPHY OF CHEMISTRY, 1492–1902. By HENRY CARRINGTON BOLTON. Second Supplement. Smithsonian Miscellaneous Collections. Part of Vol. XLIV. Washington: Smithsonian Institution. 1904. pp. 462.

Dr. Bolton's premature death occurred while this work was in the press, consequently Mr. Axel Moth compiled the index and prepared most of the proof. The original volume appeared in 1893; the first supplement, published in 1899, included the literature from 1892 to the close of 1897; the present volume brings it down to the end of 1902. No attempt has been made to index books and periodicals, but the titles of books are given under the following heads: (I.) Bibliography, (II.) Dictionaries, (III.) History, (IV.) Biography, (V.) Chemistry, pure and applied, (VI.) Alchemical literature of the nineteenth century, (VII.) Periodicals, (VIII.) Academic dissertations. The volume shows evidence of the painstaking care characteristic of Dr. Bolton's work and will, undoubtedly, be of considerable utility to many chemists.

J. B. T.

DIE WISSENSCHAFTLICHEN GRUNDLAGEN DER ANALYTISCHEN CHEMIE. Elementar dargestellt von W. OSTWALD. Vierte auflage. Leipzig: Engelmann. 1904.

Prof. Ostwald's valuable little book has appeared in English, Russian, Italian, Hungarian, Japanese and French translations. It would be superfluous to add anything to what has been said of it in the review of the first edition[2] and the review of M'Gowan's translation.[3]

E. R.

[1] Rec. Trav. Chim., **24**, 105 (1905).
[2] THIS JOURNAL, **16**, 564.
[3] *Ibid.*, **18**, 523.

OUTLINES OF PHYSIOLOGICAL CHEMISTRY. By S. P. BEEBE, PH.D., Physiological Chemist to the Huntington Fund for Cancer Research, and R. H. BUXTON, M.D., Professor of Experimental Pathology, Cornell Medical College. New York: The Macmillan Company. 1904. pp. 194. Price, $1.50.

This book was intended to fill a gap left by the laboratory manuals and was written to aid the student in grasping the theoretical aspect of physiological chemistry. That there is a place for such a book the reviewer does not deny, but that the present effort is certainly not a successful one is beyond question. In a few pages are considered: The Theory of Solutions (22 pp.); Organic Chemistry (77 pp.); The Proteids (61 pp.); The Enzymes (15 pp.); Diseases and Immunity (16 pp.). The authors explain the use of the tartrate in Fehling's solution as follows: "To avoid this, tartaric acid is used, which forms a soluble colorless (?) compound with the cupric oxide but does not affect the red cuprous oxide. The point is to add something by which the CuO is made soluble and colorless, but which leaves the Cu_2O unchanged."

On page 174 the statement is made that the oxygen, liberated from oxyhaemoglobin, is atomic and not molecular oxygen. Innumerable other examples might be given but they all show the same thing. If the contents of the book had been better it would have deserved a better style. The fact that the authors state in the preface that they hope no errors had been committed, proves that this was not sufficient to exclude them.

A. S. L.

NOTES ON ASSAYING AND METALLURGICAL LABORATORY EXPERIMENTS. By RICHARD W. LODGE. New York: John Wiley & Sons. 1904. 8vo. pp. viii + 287. Price, $3.00.

The topics considered are: Reagents, furnaces, crucibles, etc.; Sampling; The assays of ores of silver, of gold, of lead; The assay of bullion; The assay of ores of copper and tin; Platinum and the platinum group; Metallurgical laboratory experiments and notes.

The book, as a whole, is a valuable addition to the existing literature on assaying, which is, as defined by the author, a branch of analytical chemistry. It will prove of use to practical assayers and will tend to make them discard the rule-of-thumb methods which have too long prevailed. As a textbook the arrangement of the subject-matter is bad; silver in ores is treated in a separate chapter from gold in ores; copper matte is the first assay given in detail; the assay of bullion is placed between the assay for lead and for copper, etc. Many valuable tables are given, such as the losses of silver in cupellation at different temperatures. The explanations of the ef-

fect of fluxes, especially the use of iron in crucible assays and the addition of silica in scorification, are excellent. Many points admit of criticism, such as the inclusion of the scorification method for telluride ores and the Cornish method for copper, with the exclusion of the Gay-Lussac method for silver bullion. Experiments by students are given in tiresome detail, often without any particular conclusions being drawn from them, while the journal articles, on similar lines, are ignored. Though many of the subjects treated in the old works on assaying are very properly omitted, some, of importance at present, such as corrected assays, the sampling of pig copper and the assay of cyanide solutions, are not adequately treated. E. H. M.

A LABORATORY CHEMISTRY. By RICHARD B. MOORE, Instructor in Chemistry, University of Missouri. Philadelphia: J. B. Lippincott Co. 1904.

This is a little manual intended for use in high schools. In the preface the author says: "In some of our states the text-books in chemistry, prescribed by law for the secondary schools, are extremely unsatisfactory. In such cases a laboratory manual that is a little more than a laboratory manual will have a distinct use." It is largely for this reason that the chapters on theory have been introduced.

The selection of experiments is judicious and the explanatory text is clear and simple. E. R.

HIGH-TEMPERATURE MEASUREMENTS. By H. LE CHATELIER and O. BAUDOUARD. Authorized translations and additions by G. K. BURGESS. Second edition, revised and enlarged. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1904. pp. 341. Price, $3.00.

The appearance of the English translation of this book has already been referred to.[1] The second edition contains new matter pertaining to Optical Pyrometry, Electrical Resistance and Thermoelectric and Gas Pyrometry. The translator states that brief descriptions have been added of some other pyrometers which have been considerably used in the industries, especially in the United States. The importance of standardizing pyrometers has been emphasized by a special chapter devoted to that subject. H. C. J.

THE ELECTRIC FURNACE. By HENRI MOISSAN, Membre de l'Institut, Professor of Chemistry at the Sorbonne. Translated by A. T. DE MOUILPIED, B.Sc. (Lond.), M.Sc. (Vict.), PH.D., Assistant Lecturer in Chemistry in the University of Liverpool. London: Arnold; New York: Longmans, Green & Co. 1904. Price, $2.75.

A review of Dr. Victor Lenher's translation of Moissan's

[1] THIS JOURNAL, 27, 235.

"Four Electrique" appeared quite recently,[1] so that further discussion of Moissan's book is unnecessary and attention may be confined to the respective merits of the translations.

Even a very superficial examination leads to the conclusion that Dr. de Mouilpied writes better and clearer English than Dr. Lenher and, on closer observation, we find that some passages, which were obscure in Lenher's translation, have lost their obscurity in that of Mouilpied. Both translations are authorized and prefaced by Moissan. The English book has better type and paper than the American. E. R.

DIE DARSTELLUNG DES ZINKS AUF ELECTROLYTISCHEN WEGE, mit 59 Abbildungen. By DR. EMIL GÜNTHER. Leipsic: W. Knapp. 1904. pp. xii + 246. Price, M. 10.

This book forms Volume XVI. of the "Monographs on Applied Electrochemistry," edited by V. Engelhardt, chief engineer and chief chemist of the firm of Siemens and Halske. The author, well known by his papers on electrometallurgical subjects, has had practical experience in the electrolytic treatment of zinc ores and is, therefore, well fitted to write upon the subject.

In the preface he briefly reviews the history of the electrometallurgy of zinc. Although many investigations were carried out during the years 1880–1895, to find new methods and to perfect old ones, the interest seems to have lagged since that time and to-day there is only a single plant in active operation.[2] While the difficulties that have to be overcome are much greater than those encountered at first in the electrolytic refining of copper, the author believes that, with a more intelligent application of physical chemistry to metallurgical problems than has been so far the case, there will come a brighter future for the electrometallurgy of zinc. While this is to be hoped for, the main obstacle to the prospect lies in the advance that has been made in the mechanical concentration of ores.

A closer study of the principles of regular wet ore-dressing has resulted in the construction of improved machinery and magnetic concentration has become an important factor in the treatment of mixed sulphide ores; static machines, of much promise, are coming into use and, more recently, acid treatment, combined with flotation, is making available immense heaps of ores which have been thrown over the dump as waste material. If the prospects for the electrometallurgy of zinc are not very brilliant, this mode of treatment may find more application than at present in special cases with ores, while

[1] THIS JOURNAL, 33, 406.
[2] Brunner, Mond & Co., Northwich, England.

electrolytic refining of crude zinc will hardly be revived. It is of value, however, to have a book devoted to the subject.

In the introduction (pp. 1–20) there are discussed, briefly, the properties, statistics and uses of zinc and the common methods of smelting its ores. The electrolytic chapter has wet (pp. 24–180) and dry (pp. 180–208) treatment as its two main divisions. Under wet electrolysis there are two classes of processes, those in which the anode energy is utilized and those in which it is not; under dry electrolysis, the divisions are preparation of electrolyte and form of apparatus. Under each head there have been assembled the various processes that have been patented or carried out more or less experimentally. Each is briefly criticized, as far as this is possible from the available data. The Hoepfner chloride process, the only one that has any commercial interest at present, occupies 91 pages of the 150 given to wet electrolysis. The discussion is of special value, as the author was actively engaged in carrying out this process in Germany. The appendix (pp. 211–241), giving an estimate of the cost of a Hoepfner plant and the cost of working, has value in that it furnishes an excellent basis for making similar estimates for other countries.

The book does not aim to discuss the principles of the electrodeposition of zinc; it treats of processes and, incidentally, in its *critique* applies the general principles and explains the difficulties. The general arrangement is good, the matter is clearly presented, references are given to sources of information, there is an excellent table of contents and a satisfactory index. The book is well printed and can be recommended to all interested in the subject. H. O. HOFMAN.

THE BECQUERREL RAYS AND THE PROPERTIES OF RADIUM. By HON. R. J. STRUTT, Fellow of Trinity College, Cambridge. London: Eduard Arnold. 1904. pp. 214. Price, $2.40, net.

This is an admirable book on radio-activity, from the semi-popular standpoint. The author states in his preface that "In writing this book my object has been to give as clear and simple an account of the phenomena of radio-activity as the subject admits of, without sacrificing accuracy. The extraordinary properties of radium have excited general interest outside the scientific world and there are probably many who would be glad to learn something of the subject, if they could find it explained without the use of technicalities However essential mathematical methods may be in developing the subject, they are seldom really necessary in presenting the results. Moreover, some idea of the train of reasoning can generally be given in ordinary language."

This gives an admirable idea of the aim of the work. The scope is fairly comprehensive, including chapters on: Electric Discharge in High Vacua, Discovery of Radio-Activity, The Properties and Nature of the Radiations, Absorption and Ionization, The Changes Occurring in Radio-active Bodies, Radio-activity in the Earth and in the Atmosphere, the Ultimate Products of Radio-active Change and The Electrical Theory of the Nature of Matter.

The book contains three appendices. The first describes a number of interesting and important experiments. The second is a brief theoretical discussion of the Theory of the Magnetic and Electrostatic Deflection of the Cathode Rays, or the β-Rays of Radio-active Substances. The third appendix deals with the treatment of pitchblende residues on a large scale.

The book is written in an enthusiastic and attractive style and holds the interest of the reader from beginning to end. A few sentences, however, could be revised advantageously, from the standpoint of English. On page 14 we read "and it is not possible to measure the electric charge of the cathode particles in a vacuum tube *either*." On page 99, "The most that can be done is to apply an electric force large enough to *snatch* practically all the ions, etc." On page 142, "clay soils are usually the most active, but Professor J. J. Thomson has found the sand from the beach at Whitby to be very active *too*."

There will doubtless be a large demand for the book, on account of the general popular interest in the subject and because it comes from an authoritative source. H. C. J.